OPTIMIZATION OF AN ACID DIGESTION FOR HFSE ANALYSES USING ICP-MS; APPLICATION TO THE ASSESSMENT ON ENVIRONMENTAL MOBILITY OF HFSE AND REE IN IRON ORE TAILINGS

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Optimization of an Acid Digestion for HFSE Analyses using ICP-MS; Application to the Assessment on Environmental Mobility of HFSE and REE in Iron Ore Tailings

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To my parents and brother,

and the rest of my family

in Peru, Heaven,

and

in the United States of America

who always support me.

Abstract

A method to optimize an acid digestion procedure for High Field Strength Elements (HFSE) was developed, using mine tailing samples of variable ages (0-10 years old), provided by Iron Ore Company of Canada (IOC). The study included experiments that aimed to find the optimal length of digestion to obtain improved recoveries for HFSE. Different acid mixtures were tested in an attempt to accomplish better digestion of the samples, and to obtain a more stable solution. For the purpose of this research, a stable solution is defined as a solution that would maintain analytes in solution over time. This study concluded that the initial parameters of the acid digestion procedure were the most effective.

The method development generated large data sets for the elements determined using this procedure. These data were analyzed to assess the environmental mobility of HFSE and REE in the samples. Samples had low concentrations of HFSE and Rare Earth Elements (REE) elements (i.e, Zr 5 ppm, Nb 1.7 ppm, Hf 0.1 ppm, etc). These tailing samples were exposed to weathering since their generation and stored in a dump, located in Labrador. The mobility investigation consisted of exhaustive comparisons of sample elemental concentrations plotted according to their ages. Unexpected variations, suggested the use of different ores or gain/loss of mass that would concentrate/dilute these elements. To understand these variations, sample concentrations were normalized, displaying parallel trends similar to igneous or sedimentary rocks. From these observations, it was concluded that HFSE or REE were not selectively affected during weathering and ores with common HFSE and REE characteristics were used.

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List of Abbreviations

Alm	Almandine
Bt	Biotite
Cb	carbonate
cP	centiPoise
Fs	Ferrosilite
Grt	Garnet
Gt	Goethite
Hem	Hematite
HREE	Heavy Rare Earth Elements
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LREE	Light Rare Earth Elements
L.D.	Limit of Detection
Lm	Limonite
Mag	Magnetite
n.d.	not determined
Pa	Pascal
Qtz	Quartz
Rt	Rutile

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Chapter 1

Scope and Objectives of the Study

1.1 Introduction

The inductively coupled plasma mass spectrometer (ICP-MS) is a powerful analytical tool for trace-element determinations in Earth Science, and is especially useful in environmental geochemical analysis (Jenner et al., 1990). In the last decade, its use has increased and several systematic improvements in this instrument have been developed. These improvements included increased sensitivity, higher sample throughput, and multi-element capability. These improvements, as well as the instrument requirement to introduce the sample in solution, create a demand for continuous optimization in sample preparation; however, this demand has been neglected. The Department of Earth Sciences at Memorial University of Newfoundland (MUN) has historically analyzed samples by ICP-MS using several sample preparations depending upon the sample mineralogy and the elements to be determined. These sample preparation methods include sinter decomposition, high pressure acid decomposition, and open-vessel acid digestion. The existing open-vessel acid digestion procedure at MUN has never been thoroughly optimized for the analysis of high field strength elements (HFSE).

Zirconium, Nb, Hf, Ta, Tb and Th are commonly called high field strength elements (HFSE) and are known to be immobile (MacLean and Kranidiotis, 1987). That is, the initial ratio (mass concentration) of immobile elements to one another does not change when the sample is subjected to alterations. These alterations include high

temperature, high pressure, or surficial weathering. The immobile characteristic of HFSE makes them useful as geochemical tracers in Earth Science. In fact, HFSE determination can be used to recognize primary composition of variably altered geologic materials and to monitor the mass gain or loss of mobile elements during alteration processes (MacLean and Kranidiotis, 1987). In consequence, HFSE are used in Earth Sciences for studies such as characterization of mantle reservoirs, and in understanding processes involved in crustal genesis and subduction magmatism (McCulloch and Gamble, 1991; Wade and Wood, 2001; MacLean and Kranidiotis, 1987). Consequently, an accurate determination of these elements is important; however, the low concentrations in many rocks make their measurement difficult using ICP-MS (Chang et al., 2004). The determination of these elements is also difficult due to their common association with refractory minerals (heat resistant minerals which are hard to decompose by open-vessel acid digestion), as well as their complicated matrix/interference effects when in solution, and sensitivity limits of the instrument (Chang et al., 2002).

1.2 Open-vessel Acid Digestion

The open-vessel acid digestion is one of the oldest techniques of sample preparation. It involves the conversion of sample components into simpler chemical forms by applying heat and acids. In that way, the elements of interest are released from the sample and transferred into a solution for subsequent determination. This type of digestion is convenient, and has proven to be cost and labour effective. In addition, acid digestion is easily automated, since its operational parameters such as time, temperature,

and mixture of acids lend themselves to straightforward control. Thus, high purity acids are readily purchased or purified in-house (Taylor, et al., 2002). For these reasons and because the existing acid digestion procedure at MUN has never been thoroughly optimized, the acid digestion procedure was studied as part of this graduate research.

The open-vessel acid digestion package, currently used in the Department of Earth Sciences at MUN, involves a digestion using nitric (HNO_3), hydrofluoric (HF), boric (H_3BO_3), and oxalic ($H_2C_2O_4$) acids (Diegor et al., 2001). This procedure is simply known as acid digestion and it is generally recommended for the analysis of rocks of basaltic composition. The elements that can be determined in this package are: REE (La, Ce, Pr, Nd, Sm, Eu, Tb, Gd, Dy, Ho, Er, Yb, Lu), Y, Hf, Nb, Zr, Ta, Rb, Sr, Li, Mo, Bi, Tl, Ba, Cs, Th, U, and Pb (Longerich et al., 1993b). This digestion appears to work for most samples; however, in some cases difficulties are observed. For example, maintaining HFSE in solution, long term stability of the solution, losses due to volatilization, and the lengthy time for digestion are potential problems when refractory minerals are involved (Diegor, 1999). For the purposes of this research, a stable solution is defined as a solution in which the elemental concentration does not vary for a time period (two months or more) after being subjected to acid digestion. A better understanding of HFSE solution chemistry is needed in order to prevent precipitation and loss of HFSE during sample preparation, which is an important concern in the present study.

The Department of Earth Sciences at MUN also recommends analyzing samples using a pressed powder X-Ray Fluorescence (XRF) spectrometry procedure when analyzing samples using acid digestion. Analyses by XRF, are used as a quality control

measure because they do not require sample dissolution; therefore, it serves to identify problems associated with incomplete digestion of solid samples (Longerich et al., 1990). XRF determinations are only used as a reference for more concentrated elements due to the relatively poor limit of detection (L.D.) for some trace elements in geological samples such as Y, Zr, and Nb (Fitton, 1997). That is, ICP-MS is more sensitive than XRF. Yet, special attention is given to the comparison of the results for the elements Rb, Sr, Y, Zr, and Nb. These elements are generally difficult to decompose using acid digestion, generating lower recoveries in the analyses. Therefore, in samples with high concentrations of Rb, Sr, Y, Zr, and Nb, a good agreement in XRF and ICP-MS indicates that good dissolution was obtained by the open-vessel acid digestion technique (Longerich et al., 1993a; Taylor, 2002).

1.2.1 Detailed Acid Digestion Protocol used at MUN

As previously mentioned, the acid digestion procedure involves the conversion of sample components into simpler chemical forms by applying heat and acids. In the protocol used at MUN, a screw-top Teflon container is used and it remains loose and unsealed throughout the digestion. This type of container is used because its cap minimizes the evaporation of the solution, ensuring proper digestion. In this open vessel procedure, an accurately-weighed sample of approximately 0.1 g is digested in two cycles of a three day digestion with 2 mL of 8M HNO_3, and 1 mL of concentrated HF, at 70°C. This step is followed by evaporation to dryness at the same temperature, in order to remove Si and F from the solution (See section 2.2.1 Hydrofluoric Acid). Before the

evaporation, the screw cap is removed and rinsed with approximately 1 mL of 8M HNO_3 into the Teflon container. Two cycles are used in order to ensure a more complete digestion.

After the second digestion cycle is completed, the sample is treated with 2 mL 8M HNO_3 and 1 mL 0.453 M H_3BO_3, followed by a third evaporation to dryness. Subsequently, the sample is allowed to cool and 2 mL 8M HNO_3 are added to continue a fourth evaporation. After the final evaporation, 2 mL of 8M HNO_3 are added and the cap is loosely attached. The sample is placed on the hot plate to dissolve the residue. This solution is transferred to a clean, dry, labelled, and weighed 120 mL snap-seal container. Then 1.3 mL 0.222M $H_2C_2O_4$ and 0.665 mL HF/ H_3BO_3 (0.113M HF/0.453M H_3BO_3) acids are added. The sample is made up to a final weight of approximately 60 g with nanopure water, and the weight is recorded. Finally, the sample is diluted 20X and analysed by ICP-MS. See Appendix 1 for a flow sheet of this procedure.

1.3 High Field Strength Elements

Zirconium, Nb, Hf, Ta, and Th are elements commonly referred to as high field strength elements (HFSE) because of their high ionic potential, which is often higher than two. The ionic potential is simply defined as the ratio of the valence to the ionic radius of an element. Therefore, HFSE are small but highly charged ions (Rollinson, 1993). A brief description of these elements follows.

1.3.1 Zirconium and Hafnium

Zirconium and Hf are transition metals that occur extensively but in small concentrations in the Earth's crust, 190 ppm and 5.3 ppm, respectively (Dasch, 1996). They are never found as free metals, but are commonly found together in the mineral zircon ($ZrSiO_4$). Zircon is common in silica-rich igneous rocks, especially granites and granite pegmatites, as well as in beach sands rich in heavy minerals. The Hf/Zr ratio is about one to fifty in natural materials (Dash, 1996).

Zirconium and Hf share similar behaviour; for example, both elements are corrosion and acid resistant. They are best dissolved in HF, where the formations of anionic fluoro-complexes are important for the stabilization of the solutions. However, there are differences in solubilities and volatilities of their compounds (Cotton and Albert, 1972). Because of these chemical properties, both metals are commonly used in the construction of parts for nuclear power plants. These elements are also used to increase the melting points of high temperature ceramics (Cotton and Albert, 1972).

1.3.2 Niobium and Tantalum

Niobium and Ta are transition metals with similar chemical characteristics including high melting points and acid resistance. These elements are never found as native elements, although minerals that contain Nb also contain lesser amounts of Ta.

Due to being corrosion resistant, niobium is primarily used in special steel alloys as well as in welding, nuclear industries, electronics, optics, and jewellery. Tantalum is also corrosion resistant as well as a good conductor of heat and electricity. For this

reason, tantalum's major use involves the production of electronic components such as capacitors for portable telephones and high melting point alloys for the manufacture of jet engine components, chemical process equipment, nuclear reactors, and missile parts. Niobium and Ta are mined in several places in the world. For example, Nb is mined in Brazil, Canada, Nigeria, and Zaire, while Ta is mined in Australia, Thailand, Nigeria, Canada, and Zaire (Dash 1996).

1.3.3 Thorium

Thorium (Th) is a transition metal that occurs naturally in Earth's crust. Some isotopes of Th are radioactive with a long half-life. Thorium is commonly found as a trace element in soils and rocks. Thorium is primarily found in minerals such as monazite, and in some alkaline igneous rocks such as carbonatites. Major reserves are located in the Unites States and Brazil. Although Th is relatively abundant in Earth's crust and it has some industrial applications, exploration for Th is infrequent due to relatively low demands. Thorium is used in the production of alloys with high melting points and is being considered as an alternative nuclear fuel because it is more abundant than U (McNeil, 1991).

1.4 Rare Earth Elements

The Rare Earths Elements (REE) are an important group of trace elements in geochemistry due to their coherent behaviour as a group. The REE that can be determined at MUN by ICP-MS using acid digestion are: La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er,

Yb, and Lu. All the REEs are trivalent under most geological circumstances (the exceptions are Ce which can be 4+ and Eu which can be 2+), and their ionic radius decreases in an unusual systematic fashion with increasing atomic number, so-called "lanthanide contraction" (Dash, 1996). Also, most of the REEs are lithophile and refractory elements, with Ce, Eu and Yb less refractory than other REE (Marshall and Fairbridge, 1999).

1.5 Mine Tailings and Environmental Mobility

Mine tailings are the remaining waste material generated as a by-product, when extracting metals from an ore (Wyman and Stevenson, 2001). Therefore, mine tailings consist of rock material that has little economic mineral content (Ashworth and Little, 2001). After their generation, tailings are frequently disposed in tailing dumps. In these dumps, tailings are exposed to weathering, where they may breakdown, reducing their size to smaller masses, facilitating their mobilization by air, water, or ice (Conte, et al., 2001).

Tailings may be affected by physical and/or chemical weathering. If affected by physical weathering, tailings may breakdown into constituent minerals or particles. The principal sources of physical weathering are thermal expansion and contraction of rock, pressure release upon rock by erosion of overlying materials, and alternate freezing and thawing of water between cracks and fissures within rock (Dash, 1996). Tailings may also be affected by chemical weathering, which is a decomposition process where the

chemical composition of the minerals is altered. This type of process requires the presence of water and its reaction rate is controlled by water abundance (Dash, 1996).

The overriding factor that governs weathering processes is climate. Climate controls the type and rate of weathering by affecting the likelihood of freeze–thaw cycles and chemical reactions (Conte, et al., 2001). Chemical weathering is more likely to occur in humid tropical climates, while physical weathering from freeze–thaw cycles is more likely to take place in sub-Arctic climates (Wyman and Stevenson, 2001). Also, the mineralogical composition and texture of a rock determines the rate of weathering. Fine-grained rock will usually be more susceptible to chemical alteration but less susceptible to physical disintegration (Dash, 1996).

When exposed to weathering, mine tailings constitute a potential ecological hazard because the elemental components can be mobilized into the environment easily and therefore they may cause adverse effects (Luoma and Rainbow, 2008). For example, tailings dumped on the land may disturb and pollute surface water and smother vegetation. Also, environmental mobility caused by rainwater may transport toxic elements, especially metals, contaminating soils or surface and/or groundwater (Lu et al., 2005). For instance, coal operations often generate tailings that are acidic and their leachate can destroy aquatic ecosystems. In addition, tailings from taconite (fine-grained, weakly metamorphosed iron formation with approximately 25-30% Fe) operations may carry asbestos that can make its way into drinking-water intakes (Berndt and Brice, 2008).

1.5.1 Mine Tailing Samples from IOC

The mine tailing samples used in this research were provided and sampled by Iron Ore Company of Canada (IOC), who supported this research. IOC is the largest iron ore producer in Canada and is a world leader in the supply of iron ore pellets and concentrates. The mine and processing facilities are located in Labrador City in the province of Newfoundland and Labrador. These facilities are known as the Carol Project, where IOC started its iron ore production in 1962. The annual mine production at the open-pit operation varies from 35 to 38 million tonnes with a mean grade of 40% iron. The annual production capacity of the Carol concentrator is 17 million tonnes of iron ore concentrate, of which 13 million tonnes is pelletized and the balance is processed into several grades of concentrate products (Iron Ore Company of Canada, 2007).

The Carol Project is located in an extensive area of Proterozoic rocks, which traverse the Quebec-Labrador Peninsula for 1100 km. This area, also known as the Labrador Trough, contains three main types of iron ores: soft iron ores, taconites, and more intensely metamorphosed iron formations. The soft iron ores are mainly composed of friable fine-grained secondary iron oxides, including hematite, goethite, and limonite. The taconite formations, also known as magnetite iron formations, are fine-grained, weakly metamorphosed with high average magnetite content. The more intensely metamorphosed iron formations are mainly composed of coarse-grained hematite and magnetite. The hematite is also associated with other minerals including: grunerite, tremolite, garnet, biotite, horneblende amphiboles, actinolite and quartz (Neal, 2000).

Details about the sampling procedure employed by IOC, and the mineralogical or chemical composition of the tailings were not provided by the company. It is known that samples were taken from the mine tailings dump, where they are placed after being generated as a by-product during the Fe ore concentration operations of the mine. A brief description of the IOC extraction and concentration operations can be found in Appendix 2. It is important to note that a detailed study of these operations was not performed since it was beyond the scope of this research.

The samples from IOC were received in two batches. The first batch consisted of one sample (approximately 300 g) that was labelled as **CV-0-A** and was received in October 2007. This sample was never exposed to weathering. The second batch of tailing samples consisted of four samples and was received in December 2007. This batch included samples that were labelled **CV-0-B**, **CV-1**, **CV-5,** and **CV-10,** and were exposed to weathering (since they were generated) for less than one, one, five, and ten years, respectively. For the purpose of this research, samples are considered to be less than a year, one year, five years and ten years old (See Table 1). The quantity of each sample from the second batch (approximately 50 g) was considerably smaller than the quantity of sample in the first batch.

Table 1. Iron ore tailing samples.

Iron Ore Samples	
Name	**Description**
CV-0-A	0 year*
CV-0-B	< 1 year**
CV-1	1 year**
CV-5	5 years**
CV-10	10 years**

* As of October 2007 ** As of December 2007

It was anticipated that the tailings samples would contain HFSE and zircon crystals. This is due to the fact that most sedimentary iron formations contain detrital minerals that have the potential to contribute HFSE and zircon. Typically, the iron formations are interbedded with centimetre scale or thicker silt layers that contain erosional detritous or clastic minerals derived from surrounding regions. Whereas chemical precipitates from the water column that form iron formations are not expected to contribute heavy minerals such as zircon, the detrital erosional input into the sedimentary environment could include such minerals (Chown et. al.; 2000, Canet et. al, 2004). In this regard, samples from IOC could contain these refractory phases. It was also expected that all the tailing samples would mostly have somewhat similar mineral compositions due to the environment in which the weathering occurred. The climate in this area of Labrador can be described as Arctic and has temperatures that range from -10°C to -30°C during winter. More important to note is that Labrador has an average precipitation of 1000 mm annually and approximately 45% of this occurs as snow.

Although HFSE are considered to be immobile, it was not known how weathering could affect the geochemical composition of the fine-grained tailings supplied by IOC. In order to assess environmental mobility of the HFSE elements, the compositions of different age tailing samples (0-10 years) were compared. This study also included a determination of grain size of the tailings and heavy liquid separation. These determinations were included to determine if minerals containing HFSE were in a particular size fraction or were concentrated in the greater than 3.3 g/cm^3 density fraction.

The IOC samples were of special interest because they came from an operating mine (actively depositing tailings). In addition, weathering studies are usually done in mines that are no longer operational, where the time since depositing may not be known. Furthermore, IOC provided a sample that was never exposed to weathering and was particularly important as it provides a starting point to compare with weathered samples that were deposited later.

1.6 Objectives of the Study

The present study involved carrying out a large number of experiments that were done in order to optimize the acid digestion protocol that is used at MUN for analyzing iron ore tailings. The study consisted of testing three variables in the digestion protocol: length of digestion, the acid mixture, and stability of the resulting solution. The length of the digestion experiments aimed to find an optimal length of time for digestion that would increase the recovery of HFSE. The acid mixture experiments aimed to find an optimal acid mixture that would accomplish a complete digestion of the sample. The experiments on stability of the solution aimed to determine the most stable solution over a two month period. In the context of this research, a stable solution is defined as a solution that maintains analytes in solution over time. Therefore, the sample elemental concentration ideally should not vary after being digested. Finding a stable solution is important because in general it is not always possible to analyze a sample immediately after digestion. Delays including instrument malfunctioning or access may not permit analysis of samples immediately.

The method development to optimize the acid digestion procedure generated a large amount of data for all the elements that could be determined using this method. The data were subsequently analyzed to assess the mobility of HFSE and REE in the fine-grained mine tailing samples. As previously mentioned, samples were of different ages (0 to 10 years) and were exposed to weathering in Labrador, Canada. Although HFSE are known to be immobile, it was not known how weathering in an Arctic environment could influence mobility in these fine-grained samples. The environmental mobility assessment was done to better understand this subject. For that reason, the elemental compositions of the tailing samples can be analyzed and their results plotted according to their ages. These plotted figures can indicate if the concentration of expected immobile elements remained constant or changed with weathering time. In addition, the determined elemental concentrations of the samples can be normalized to different sets of concentrations (i.e. Primitive Mantle and/or less weathered sample). These normalizations would allow a better understanding of the elemental concentration variation in the sample.

Due to limited time and resources, this research project was restricted to the physical and chemical characterization of mine tailings samples as collected and provided by IOC. This research was not intended to study the sampling procedure employed by the company or to characterize the iron ore. It is also beyond the scope of this research to study the nature and effects of the extraction and concentration operations in the tailing samples (including milling).

Chapter 2

Literature Review of ICP-MS, Sintering, and Reagents

2.1 ICP-MS

ICP-MS is a highly sensitive analytical tool, capable of determining a wide range of elements at low concentrations, usually below one ppb (depending on the element to be determined and sensitivity of the instrument). It is generally used to determine positive ions; however, negative ions (halogens) are also produced in the plasma (Thomas, 2001a).

An ICP-MS combines the principles of an inductively coupled plasma with a mass spectrometer. An inductively coupled plasma, as the name suggests, creates a plasma, which is a gas-like phase that contains enough ions and free electrons to make the vapour phase fluid electrically conductive. Mass spectrometry separates ions formed in the plasma according to their mass/charge ratio. Then a signal, proportional to the concentration of the analyte, is detected, which leads to the determination of elemental concentrations. In general, argon is the gas of preference to create the plasma. This is due to its natural abundance, which in turn gives argon a low cost compared to other noble gases.

The most important principle in an ICP-MS is the use of a high temperature plasma discharge to generate positively-charged ions. In order to accomplish the formation of a plasma with these high temperatures, the inductively coupled plasma is

sustained through a plasma torch, radio frequency (RF) coil and RF power supply (Thomas, 2001c). Before the sample reaches the plasma, however, it goes through a series of steps. First, the liquid sample passes through a nebulizer, where it emerges as an aerosol. Then, the aerosol passes through a spray chamber in order to allow aerosol droplets to enter the plasma. These steps are fundamental because one of the instrument requirements is the conversion of the liquid sample into a fine-droplet aerosol. This is due to the fact that fine-droplet aerosols are more suitable for ionization (Thomas, 2001b). As the aerosol droplets travel to different areas of the plasma, they are vaporized and atomized. Finally, the aerosol arrives to the analytical zone of the plasma at 6000-7000 °K, where it is ionized.

After the sample is ionized, the ions are transported to the mass spectrometer. This transportation is a challenge due to the differences in pressure of the plasma (atmospheric pressure) and the mass spectrometer (10^{-6} Torr). For that reason, the ions are directed to the interface region, which consists of two metallic cones with small orifices. Consequently, the ions pass through the first cone, known as the sampler cone, which has an orifice diameter of approximately 0.8 to 1.2 mm. From there, the ions travel a short distance to the second cone also called the skimmer cone, which is generally sharper than the sampler cone and has a much smaller orifice of approximately 0.4 to 0.8 mm in diameter. The difference in the diameter of the orifices increases the vacuum in that interface. When the ions emerge from the skimmer cone, they are directed through the ion focusing system optics into the mass separation device (Thomas, 2001d).

The focusing system, also called the ion optics, focuses the ion beam into the mass analyzer. This system consists of one or more ion lenses that electro-statically direct the analyte ions into the mass analyzer (Thomas, 2001e). After being focused, the ion beam is ready to be separated according to its mass to charge ratio by the mass analyzer. The goal of this device is to separate the ions of interest from all the other non-analyte, matrix, solvent, and argon-based ions (Thomas, 2001f).

There are several types of mass analyzers; however, the most commonly used for trace elements is the quadrupole mass filter. The Department of Earth Science at MUN has an HP 4500plus ICP-MS, with this type of analyzer. The quadrupole mass filter consists of four cylindrical or preferably hyperbolic metallic rods of identical length and diameter. The basic principle of operation involves placing a combination of a direct current field and a radio frequency field on the opposite pairs of rods. Depending on the direct current and alternating current field applied to the rods, only the ions of interest are passed through the rods to reach the detector. The other ions are ejected from the quadrupole or impact on the rods. In other words, the positive or negative bias on the rods electrostatically steer the analyte ion of interest down the middle of the four rods. This process can be repeated for other analytes that have different mass to charge ratios, until the selected analytes in a multielement analysis have been measured (Thomas, 2001f).

When the ions emerge from the quadropole, they are converted to an electrical pulse by the detector. The detection system is important because it allows the counting of the electrical pulses. The number of electrical pulses is proportional to the number of analyte ions present in the sample. The signal, produced by the sample, is compared with

the ion signal of a reference standard material that is produced during the calibration of the ICP-MS. This allows the determination of the concentration of the elements (Thomas, 2001g).

The major disadvantage of the ICP-MS is the requirement to introduce the sample in solution, which brings a potential problem of incomplete dissolution (Longerich et al., 1990). For that reason, sample preparation is a critical step in the ICP-MS analytical protocol and may entail steps from simple dilution to partial or total digestion, depending on the material to be analyzed (Matusiewicz, 2003). In general, sample preparation involves the conversion of a sample into a suitable solution in order to determine elements with a variety of analytical instruments, including ICP-MS. When preparing solid samples, the original crystal structure of the mineral is destroyed and the elemental chemical form is changed. In order to select an appropriate sample preparation technique, the analyst must take into account the objective of the study as well as the chemical composition of the sample, the elements to be determined, and the precision and accuracy required (Totland et al., 1992). As a result of these criteria, there is no single decomposition technique capable of dissolving all elements from every type of geological or environmental sample (Chao and Sanzolone, 1990).

The Department of Earth Science at MUN uses three different sample preparation techniques to dissolve samples. These are: 1) sintering decomposition; 2) high pressure decomposition; and 3) open-vessel acid digestion. For solution samples, a simple dilution is usually used. In general, the sintering decomposition is used for granitic rocks (which often contain insoluble minerals such as zircon), the high pressure decomposition is used

for sediments and ores, and the open-vessel acid digestion is used for rocks of basaltic composition. A brief description of the sintering decomposition technique is shown below. This technique was used once, only as a reference point, during the course of the research. These results were compared with the acid digestion results in order to determine if complete dissolution was accomplished when using the acid digestion. Since high pressure decomposition was not used in this study, and it is beyond the scope of the research, it is not discussed in this thesis.

2.1.1 Sinter Decomposition

Sintering decomposition is a sample preparation technique that decomposes a mineral or rock at high temperatures. This method is important because the sample is not only melted and decomposed, but also the resulting cooled solid can be dissolved in water or acids. For the sintering decomposition, the sample is mixed with a flux (e.g. a salt, such as sodium carbonate or sodium peroxide). The mixing ratio and temperature varies according to the used flux (Potts, 1987).

The sintering decomposition package, employed at the Department of Earth Science at MUN, involves the use of sodium peroxide (Na_2O_2) as a flux. In this procedure, also known as the sodium peroxide sinter package, the sample is mixed with Na_2O_2 in a ratio of 4:1 (peroxide: sample), placed in a 30 mL nickel crucible, and heated at 480°C for two hours in an oven. The cooled material is a solid that is easily dissolved by water and acids (Longerich et al., 1990). The sintering decomposition is advantageous

because it uses high temperatures, which cannot be reached in acid digestions because of the low boiling temperature of the acid solution used in open digestion vessels.

In general, the sinter package is used for geological samples that contain mineral phases that are difficult to decompose using open-vessel acid digestion (such as zircons and other accessory minerals). This sintering procedure is most appropriate for rocks carrying high concentrations of trace elements in refractory minerals, found typically in granites. A refractory mineral is simply a mineral that is hard to alter or decompose. This technique produces quality data for the REE (La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, Lu) Y, Th, Zr, Nb, Hf, and Ta (Longerich et al., 1990).

One important advantage of the sintering procedure is that it can be carried out in a relatively short time with reproducible results. However, there are potential problems from reagent contamination due to the difficulty of obtaining a consistent flux quality. Also, samples are not analysed for a number of elements including Rb, Sr, Cs, U, and Pb because they are more soluble and as such are removed totally or partially in the water extraction that follows the sintering. Also, the decomposition of large number of samples by sintering is more labour intensive compared to acid digestion.

2.2 Common Acids Used in the Open-vessel Acid Digestion

2.2.1 Hydrofluoric Acid

Hydrofluoric acid (HF) is a non-oxidizing inorganic acid with a boiling point of 112°C at a concentration of 48% (Chao and Sanzolone, 1990). Hydrofluoric acid is

important in digestions because it aggressively reacts with silicate minerals. It has the ability to complex Si by breaking the Si-O bonds in the minerals. When HF reacts with silicon oxide or silicate minerals in an acid solution, the aqueous species H_2SiF_6 is formed. Subsequently, H_2SiF_6 is decomposed and removed as gas phase as silica tetra-fluoride (SiF_4):

$$H_2SiF_6 \rightarrow SiF_4\uparrow + 2\ HF \qquad (1)$$

The removal of silica tetra-fluoride is accomplished by heating the mixture (Dolezal et al., 1968). The formation of fluoride and oxyfluoride aqueous complexes also facilitates the dissolution of Nb, Ta, and W compounds and prevents the precipitation of surface-active hydrolytic products in acid solutions (Sulcek et al., 1977).

The removal of Si and F by evaporation during this procedure has several advantages. First, the solution becomes more stable because silica solutions tend to hydrolyse and precipitate amorphous silica when standing for long periods of time. Second, the HF removal makes the further manipulation of the samples easier. Third, by removing Si, the total dissolved solids (TDS) of the solution are reduced, which facilitates analysis. Fourth, the removal of Si and F reduces further mass interferences in the ICP-MS caused by the presence of these elements and their complexes (Potts, 1987). The disadvantage of HF procedures is the possibility of fluoride precipitates. In order to reduce this problem, fluorides are removed during evaporation with another mineral acid. The current acid digestion package at MUN uses HNO_3 during these HF evaporations.

Hydrofluoric acid is not usually used alone in an open vessel acid digestion because some salts such as those of K or Ca are insoluble in HF (Potts, 1987). This is why

a mixture of acids is used in order to increase the decomposition of rocks containing minerals such as carbonates, sulphides or oxides. In addition, Fe is usually present in rocks, and therefore, it is necessary to use other acids, such as HNO_3 or hydrochloric acid (HCl), for digestion of this element. These acid mixtures are also used to moderate the initial vigorous reaction when HF is used alone (Chao and Sanzolone, 1990).

2.2.2 Nitric Acid

Nitric acid, is a strong oxidizing agent, especially when concentrated and hot (Matusiewicz, 2003, p. 196-200). It is frequently used for dissolution of minerals containing polyvalent elements such as sulphides, selenides, tellurides, arsenides, and sulfoarsenides. Therefore, when HNO_3 reacts with the anionic and cationic components of the mineral, the resulting salts have, in general, high oxidation states (Sulcek et al., 1977).

Nitric acid is commonly used to decompose a number of minerals but it is not as effective as HCl in dissolving oxide minerals, especially those containing Fe or Mn (Chao and Sanzalone, 1990). A number of metals can be dissolved with HNO_3; however, this is not the case for Au and the Pt group elements (Dolezal et al., 1968). Nitric acid is widely used because many non-silicate minerals are soluble and, once dissolved, remain stable in solutions with this acid. Nitric acid is the preferred acid for ICP-MS analyses, since it avoids the addition of excess chlorine in solution, which can cause important analytical interferences with some elements (Longerich et al., 1990). It is convenient to use HNO_3 due to high purity commercial availability or ease of in-house distillation.

2.2.3 Boric Acid

Boric acid (H_3BO_3) is a relative weak acid that is soluble in hot water and stable up to 170°C. When heated above this temperature, it forms HBO_2, metaboric acid (Lewis, 2001). Boric acid is a weak acid since it does not highly dissociate in aqueous solution, but is acidic due to its interaction with water molecules. It has a tendency to form complex compounds such as boroarsenites, borotungstates, or borovanadates (Thorpe and Whiteley, 1946).

In geochemistry, H_3BO_3 is used to complex excess HF when analyzing silicate materials. With the addition of H_3BO_3, fluoroboric acid is formed in a two step exothermic reaction (Potts, 1987):

$$H_3BO_3 + 3\ HF \leftrightharpoons HBF_3OH + 2\ H_2O \qquad (2)$$

$$HBF_3OH + HF \leftrightharpoons HBF_4 + H_2O \qquad (3)$$

Complexing HF with H_3BO_3 is advantageous for several reasons. First, the resultant solution is more stable. Second, H_3BO_3 is used to dissolve relatively insoluble fluoride complexes formed during sample decomposition. Third, the resulting solution can be placed in glassware containers, since the ability to dissolve glass by HF solutions is suppressed. Thus, the solution becomes less hazardous to handle (Bernas, 1968). However, adding H_3BO_3 increases the amount of TDS, which can decrease the elemental sensitivity in some analytical instruments. The acid digestion protocol utilized at MUN involves the use of a very low concentration of H_3BO_3 such that the loss of sensitivity in the ICP-MS is not significant.

2.2.4 Oxalic Acid

Oxalic acid ($H_2C_2O_4$) is an organic dicarboxylic acid soluble in cold water (Dazeley, 1969). In analytical chemistry, $H_2C_2O_4$ is used for selective dissolution as well as a fluoride removing agent. In addition, $H_2C_2O_4$ is a reducing agent and an important ligand in coordination chemistry. Oxalic acid can form oxalates, $C_2O_4^{2-}$ or $(COO)_2^{-2}$, that react to form insoluble precipitates with some metal ions.

Adding $H_2C_2O_4$ in an analytical protocol is beneficial for the above-mentioned reasons and because its removal from solution is simple. Oxalic acid is non volatile but any excess is readily decomposed by heating because oxalates convert in solution to form carbonates (Dolezal et al, 1968). In the current analytical protocol used at MUN, 0.2M $H_2C_2O_4$ solution is added to the HF-HNO_3 mixture in the dissolution stage in order to complex Fe. Typically, Fe is complexed by HCl; however, the addition of HCl creates some undesirable polyatomic chloride ion interferences in ICP-MS. By comparison, an oxalic solution only adds insignificant carbon to the plasma and carbon is already present in the plasma due to impurities in the argon gas and from air entrainment. Therefore, $H_2C_2O_4$ does not produce significant deleterious effects on the analysis (Longerich et al., 1990).

Chapter 3

Optimization of the Acid Digestion Procedure

3.1 Preliminary Steps

A study of the acid digestion procedure and environmental mobility was done on IOC tailing samples (Table 1). Before the method development to optimize the acid digestion procedure was initiated, the tailing samples underwent a series of preliminary steps. The samples were air dried for one day and then mechanically divided in two portions using a sample splitter. One portion of the sample was stored and the other portion was pulverized to a fine powder using a tungsten carbide mill for approximately 1 minute. These pulverized samples were then used to determine chemical characteristics of the sample and to optimize the acid digestion procedure.

3.2 Chemical Characterization of Tailing Samples

A chemical characterization of tailing samples, that included X-Ray Fluorescence (XRF) spectrometry, sintering and acid digestion analyses, was done. X-Ray Fluorescence (XRF) spectrometry and sintering analyses were done only for a reference and results were later compared to the acid digestion results. This comparison would aid in determining if a complete dissolution was accomplished when using acid digestion. When a complete dissolution is accomplished, the XRF and sintering results should agree with the acid digestion results. On the contrary, if an incomplete dissolution occurs, the

acid digestion results would be lower than sintering and XRF results. Due to the fact that XRF and sintering analyses were used only as references and are not the foci of the study, as well as limited economical and time resources, XRF and sintering analyses were done once without replicates.

3.2.1 Analyses of Tailing Samples using XRF

The variably-aged tailing samples were analyzed using XRF. The results generated were used as a starting reference point when determining elements of interest using acid digestion. As previously mentioned, XRF analyses are useful because the instrument does not require introducing the sample as a solution; therefore, incomplete dissolution problems are avoided. However, XRF is less sensitive than ICP-MS and can only be used for certain elements, see Table 2 (L.D. of the XRF is higher than ICP-MS, e.g. the L.D. for Zr in XRF is approximately 1.7 ppm while in ICP-MS is approximately 0.9 ppm).

The analyses of the tailing samples using XRF, shown in Table 2, suggest that most of trace element concentrations, including HFSE, are very low compared to common rocks (the Fe concentration process might effectively remove Fe and other heavy metals, see Appendix 2). Low trace element concentrations may lend to difficulties in obtaining precise data because these concentrations would be approaching or below the L.D. of the ICP-MS.

Table 2. Analyses of tailing samples using XRF.

Mineral/ Element	Wt or ppm	L.D.*	CV-0-A n=1	CV-0-B n=1	CV-1 n=1	CV-5 n=1	CV-10 n=1
Na_2O	wt%	0.02%	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.
MgO	wt%	0.01%	2.4%	3%	5%	4%	4%
Al_2O_3	wt%	0.06%	<L.D.	<L.D.	0.13%	0.10%	0.15%
SiO_2	wt%	0.01%	78%	90%	60%	60%	70%
P_2O_5	wt%	0.004%	0.04%	0.03%	0.05%	0.07%	0.06%
S	ppm	20	159.5	150	170	150	170
Cl	ppm	36	88.39	70	116	123	90
K_2O	wt%	0.003%	0.02%	0.03%	0.05%	0.05%	0.06%
CaO	wt%	0.003%	3%	5%	7%	5%	5%
Sc	ppm	9	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.
TiO_2	wt%	0.00004	0.01%	0.01%	0.04%	0.03%	0.03%
V	ppm	7	10	12	24	17	18
Cr	ppm	8	19.82	402	476	350	353
MnO	wt%	0.002%	0.4%	0.5%	0.9%	1.0%	0.8%
Fe_2O_3T**	wt%	0.01%	15%	11%	29%	31%	23%
Ni	ppm	4	<L.D.	8	33	11	17
Cu	ppm	4	2	7	16	18	12
Zn	ppm	2.1	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.
Ga	ppm	4	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.
As	ppm	20	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.
Rb	ppm	0.9	<L.D.	<L.D.	1.17	<L.D.	1.44
Sr	ppm	1.5	7	9	15	14	14
Y	ppm	0.9	5	5	7	9	8
Zr	ppm	1.7	5	6	10	8	7
Nb	ppm	0.9	2	2	4	3	3
Ba	ppm	20	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.
Ce	ppm	40	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.
Pb	ppm	5	8	<L.D.	18	20	14
Th	ppm	4	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.
U	ppm	5	<L.D.	<L.D.	5	<L.D.	<L.D.

*L.D.: Limit of detection of the instrument. ** Fe2O3T= FeO + Fe_2O_3

3.2.2 Analyses of Tailing Samples using Sintering

Due to the fact that the XRF results suggested that concentrations of most elements were low, it was important to confirm these results by analyzing the samples using a more sensitive technique. Subsequently, the variably-aged tailing samples were analyzed by ICP-MS using sintering decomposition. Nonetheless, sintering analyses were only used as a reference to be later compared with the acid digestion results. Since sintering results were used only as a reference, no replicate analyses were done. Sintering results are shown in Table 3.

Table 3. Analyses of tailing samples using sintering.

Element	L.D. n=1	CV-0-A n=1	CV-0-B n=1	CV-1 n=1	CV-5 n=1	CV-10 n=1
Y	0.05	4.4	6.0	7.7	7.5	7.5
Zr	0.19	6.2	10.6	12.5	8.1	10.1
Nb	0.15	1.4	2.4	2.9	2.0	1.8
Ba	0.55	15	24	32	31	30
La	0.07	1.70	2.30	4.16	3.47	3.18
Ce	0.04	3.78	3.97	7.28	5.63	5.67
Pr	0.04	0.36	0.49	0.88	0.75	0.69
Nd	0.25	1.63	2.01	3.60	3.23	2.82
Sm	0.30	<L.D.*	0.39	0.67	0.64	0.50
Eu	0.02	0.13	0.18	0.28	0.27	0.25
Tb	0.002	0.08	0.11	0.15	0.14	0.14
Dy	0.05	0.57	0.87	1.00	0.98	1.05
Ho	0.01	0.15	0.20	0.25	0.25	0.23
Er	0.04	0.48	0.62	0.81	0.80	0.73
Tm	0.03	0.07	0.09	0.11	0.12	0.09
Yb	0.13	0.44	0.57	0.78	0.72	0.67
Lu	0.02	0.06	0.08	0.11	0.10	0.09
Hf	0.12	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Ta	0.26	1.10	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Th	0.06	0.18	0.14	0.27	0.10	0.17

*<L.D.: Data below limit of detection of the instrument. Concentrations in ppm

3.2.3 Analyses of Tailing Samples using Acid Digestion

The set of tailing samples was analyzed using acid digestion (see protocol's description in section 1.2.1). The summary results of these analyses are shown in Table 4 and the complete set of data are shown in Appendix 4 (see Appendix 3 to review used statistical concepts). These results were later compared with XRF and sintering results, in order to determine if the acid digestion procedure effectively dissolved the samples. From this point, several experiments were done in order to develop a method to optimize the acid digestion procedure used at MUN. Note that it was intended to analyze all samples six times; however, a malfunctioning of the ICP-MS did not allow the completion of these analyses. Since all samples were analyzed at least four times and time being a limiting factor, it was decided to continue with the next part in the research.

Table 4. Analyses of tailing samples using acid digestion (mean).

	CV-0-A					CV-0-B					CV-1					CV-5					CV-10				
Element	n	$\bar{x}$	s.d.	s($\bar{x}$)	rsd	n	$\bar{x}$	s.d.	s($\bar{x}$)	rsd	n	$\bar{x}$	s.d.	s($\bar{x}$)	rsd	n	$\bar{x}$	s.d.	s($\bar{x}$)	rsd	n	$\bar{x}$	s.d.	s($\bar{x}$)	rsd
Li	6	1.10	0.14	0.057	5.2%	4	1.35	0.64	0.318	23.6%	5	1.54	0.52	0.23	15.1%	3	0.92	0.15	0.09	9.3%	4	1.02	0.18	0.09	8.6%
Ti	6	57.2	10.4	4.228	7.4%	3	73.8	1.66	0.960	1.3%	3	199	5.89	3.40	1.7%	3	195	11.3	6.52	3.3%	3	127	13.1	7.57	6.0%
V	6	7.47	0.75	0.306	4.1%	3	10.5	0.24	0.140	1.3%	3	19	0.33	0.19	1.0%	3	16.5	1.60	0.93	5.6%	3	12.2	1.57	0.90	7.4%
Cr	3	62.2	6.79	3.923	6.3%	3	335	5.56	3.208	1.0%	3	442	7.08	4.09	0.9%	3	279	9.72	5.61	2.0%	3	267	39.5	22.81	8.5%
Rb	4	1.33	0.40	0.199	15.0%	3	0.54	0.13	0.073	13.5%	4	0.92	0.07	0.04	3.9%	3	0.88	0.15	0.09	9.8%	4	1.15	0.21	0.10	9.0%
Sr	5	6.13	0.77	0.342	5.6%	3	9.01	0.43	0.250	2.8%	5	14.3	0.67	0.30	2.1%	4	12.4	0.55	0.28	2.2%	4	11.3	0.59	0.29	2.6%
Y	6	4.03	0.14	0.058	1.4%	4	3.91	0.22	0.108	2.8%	5	6.54	0.21	0.10	1.5%	4	6.45	0.27	0.13	2.1%	4	5.57	0.26	0.13	2.3%
Zr	6	4.95	0.90	0.367	7.4%	4	5.23	0.28	0.139	2.7%	3	7.33	1.21	0.70	9.6%	4	5.14	0.71	0.35	6.9%	4	4.57	0.69	0.34	7.5%
Nb	6	1.66	0.09	0.038	2.3%	4	2.13	0.18	0.088	4.2%	5	2.65	0.33	0.15	5.5%	4	1.73	0.17	0.09	4.9%	4	1.51	0.11	0.06	3.6%
Mo	4	1.37	1.06	0.532	39.0%	4	3.50	0.61	0.303	8.7%	5	4.52	1.08	0.48	10.6%	4	4.29	0.43	0.21	5.0%	4	2.76	0.54	0.27	9.8%
Cs	3	0.38	0.04	0.021	5.7%	0	<L.D.*									0	<L.D.*				0	<L.D.*			
Ba	6	10.02	4.27	1.744	17.4%	4	13.51	1.35	0.677	5.0%	5	18.31	0.48	0.21	1.2%	4	19.69	3.21	1.61	8.2%	4	17.6	1.42	0.71	4.0%
La	6	2.05	0.53	0.216	10.5%	4	2.19	0.19	0.093	4.2%	5	3.86	0.09	0.04	1.0%	4	3.40	0.24	0.12	3.5%	4	2.90	0.29	0.15	5.1%
Ce	6	4.24	0.87	0.354	8.4%	4	3.79	0.26	0.130	3.4%	5	6.65	0.15	0.07	1.0%	4	5.51	0.42	0.21	3.8%	4	5.22	0.47	0.24	4.5%
Pr	6	0.46	0.12	0.051	11.1%	4	0.52	0.06	0.028	5.5%	5	0.86	0.02	0.01	1.0%	4	0.76	0.03	0.01	1.8%	4	0.67	0.07	0.03	5.0%
Nd	6	1.91	0.56	0.229	12.0%	4	2.15	0.10	0.048	2.3%	5	3.41	0.14	0.06	1.8%	4	3.23	0.11	0.05	1.7%	4	2.73	0.28	0.14	5.1%
Sm	3	0.45	0.10	0.059	13.1%	4	0.45	0.03	0.016	3.6%	5	0.72	0.06	0.03	3.9%	4	0.69	0.08	0.04	6.1%	4	0.57	0.07	0.03	5.8%
Eu	6	0.17	0.04	0.018	10.6%	4	0.17	0.01	0.007	3.8%	5	0.26	0.02	0.01	2.7%	4	0.25	0.03	0.02	6.9%	4	0.22	0.03	0.01	6.8%
Gd	6	0.53	0.06	0.023	4.3%	4	0.52	0.01	0.006	1.1%	5	0.80	0.03	0.01	1.5%	4	0.78	0.05	0.03	3.5%	4	0.73	0.04	0.02	2.4%
Tb	6	0.08	0.02	0.007	8.8%	4	0.08	0.004	0.002	2.4%	5	0.13	0.01	0.003	2.3%	4	0.14	0.02	0.01	8.0%	4	0.11	0.01	0.01	5.9%
Dy	6	0.57	0.08	0.031	5.5%	4	0.58	0.02	0.011	1.8%	5	0.92	0.05	0.02	2.2%	4	0.90	0.08	0.04	4.3%	4	0.81	0.06	0.03	3.8%
Ho	6	0.13	0.02	0.007	5.0%	4	0.12	0.00	0.002	1.5%	5	0.21	0.02	0.01	5.2%	4	0.20	0.01	0.01	3.6%	4	0.18	0.01	0.01	4.0%
Er	6	0.43	0.08	0.031	7.2%	4	0.40	0.04	0.020	5.1%	5	0.66	0.05	0.02	3.5%	4	0.65	0.05	0.03	4.1%	4	0.57	0.05	0.02	4.1%
Tm	6	0.07	0.02	0.009	12.6%	4	0.08	0.02	0.010	12.8%	5	0.12	0.02	0.01	7.6%	4	0.11	0.02	0.01	7.4%	4	0.10	0.02	0.01	8.5%
Yb	6	0.43	0.09	0.035	8.2%	4	0.39	0.03	0.014	3.5%	5	0.63	0.02	0.01	1.3%	4	0.63	0.05	0.03	4.0%	4	0.54	0.05	0.02	4.3%
Lu	6	0.06	0.01	0.005	8.5%	4	0.05	0.01	0.003	5.8%	5	0.08	0.00	0.001	1.4%	4	0.08	0.01	0.004	5.4%	4	0.07	0.01	0.003	4.7%
Hf	1	0.14				1	0.14				2	0.50	0.11	0.07	14.9%	1	0.76				1	0.30			
Ta	6	1.59	0.04	0.017	1.1%	1	0.03				2	0.04	0.00	0.003	8.2%	1	0.03				0	<L.D.*			
Tl	0	<L.D.*				0	<L.D.*				2	0.04	0.00	0.001	1.7%	0	<L.D.*				0	<L.D.*			
Pb	2	1.07	0.76	0.540	50.4%	4	0.61	0.11	0.054	8.7%	4	0.62	0.11	0.05	8.5%	1	0.40				1	0.46			
Bi	1	0.08				3	0.10	0.02	0.009	8.3%	2	0.03	0.01	0.004	11.8%	3	0.13	0.03	0.02	14.9%	0	<L.D.*			
Th	6	0.09	0.02	0.010	11.1%	4	0.09	0.02	0.010	11.2%	5	0.22	0.02	0.01	4.6%	4	0.12	0.03	0.01	11.7%	3	0.11	0.03	0.02	14.4%
U	6	0.07	0.02	0.008	11.3%	1	0.03				4	0.09	0.01	0.01	8.5%	1	0.04				3	0.05	0.004	0.002	3.7%

This table shows the number of times that a sample was analyzed (n), the calculated mean of the sample elemental concentration ($\bar{x}$) in ppm, the standard deviation of the sample (s.d.), the standard deviation of the mean (s($\bar{x}$)) and the relative standard deviation of the mean (rsd). *<L.D.: Data below limit of detection of the instrument.

3.2.4 Comparison of Analytical Methods

As previously mentioned, the tailing samples were analyzed through three different methods: XRF, sintering, and acid digestion. The XRF and sintering analyses were used only as a reference and these results were compared with the acid digestion results. In order to aid in the comparison and to improve the graphical presentation, the data generated by the acid digestion, XRF, and sintering were normalized to the Primitive Mantle (PM). The normalization of the samples consisted of systematically dividing each of the element concentrations in the tailing samples by the concentration of the same element in a reference material. In this case, the reference material used was PM, which is a set of values that represents the estimated composition of the Earth's mantle before the separation of the continental crust formation; see Appendix 5 (Rollinson, 1993). It is important to note that the analysis of the tailings yielded a variety of elemental concentrations with different abundances, which required plotting in order to better interpret the data. These abundances varied from a fraction of a ppm to hundreds of ppm or even percents. Thereby, the plotted diagrams would show several peaks and troughs corresponding to the widely varying concentrations, which made the comparison difficult. When the composition of the samples was normalized to the PM and the elemental ratios were plotted, peaks and troughs on the multi-element diagrams largely disappeared. These normalized ratios were plotted on a semi-logarithmic scale; therefore, the simultaneous, multi-element comparison of the compositions of several samples became much easier. The data could be normalized to the least weathered sample (CV-0-A);

however, the data were not normalized to CV-0-A because if anomalies existed in the mine tailing samples, this graph would not illustrate them.

Figures 1 to 10 show the comparisons of the results produced in the analyses of each sample (CV-0-A, CV-0-B, CV-1, CV-5, and CV-10) using acid digestion and XRF, as well as using acid digestion and sintering. In these Figures, the XRF data are plotted in blue, the acid digestion data are plotted in red, and the sintering data are plotted in black. Note that the graphs used the mean of the results produced using acid digestion. It is important to note that although samples were analyzed a number of times, some elemental concentrations were below the limit of detection of the method.

The elements that could be determined and compared by both XRF and acid digestion are: Rb, Sr, Y, Zr, and Nb. The elements that could be determined and compared using sintering and acid digestion were: Y, Zr, Nb, La, Ce, Pr, Nd, Sm Eu, Tm, Yb, Lu, Hf, Ta, and Th. Note that Rb and Sr as well as Cs, U and Pb are not analyzed by sintering because they are removed totally or partially in the water extraction that follows the sintering. Subsequently, these elements can not be compared with the acid digestion results. It is also important to note, that both the sintering and acid digestion protocols produced results for Ba; however, the results by sintering are monitored only to correct the Ba interference on Eu, since there is a partial loss of Ba in the sinter preparation procedure. Therefore, the Ba results were not used in these comparisons.

As previously stated, samples were analyzed once using XRF and sintering and the results were used only for comparison. Therefore, there were not enough data to perform an in-depth statistical analysis. Note that the figures showing samples analyzed

by sintering decomposition have 5% fixed error bar (1 σ). This value was used because long term (non-published) data acquisition of sintering analyses (generated in the Department of Earth Science at MUN) have revealed that this type of sample preparation has a precision of 5% r.s.d. (H. Longerich, personal communication, February 3, 2009). It can also be observed that the figures showing samples analyzed by acid digestion are presented with error bars. The error bars on the acid digestion plots were calculated by multiplying the r.s.d. (see Table 4) and the normalized PM elemental concentration.

Figures 1 and 2 suggest that CV-0-A elemental concentrations determined through acid digestion, sintering and XRF are very close to each other. For that reason, this characterization suggested that CV-0-A does not contain difficult to digest refractory phases. It is important to note that Zr concentrations, determined through acid digestion and XRF are almost identical. Thus, Zr concentrations, determined through acid digestion are lower than Zr concentrations determined through sintering. On the other hand, Figures 3 to 10 showed that Zr concentrations determined through acid digestion in samples CV-0-B, CV-1, CV-5 and CV-10 are lower than the Zr concentrations analyzed by XRF or sintering. In other words, the chemical characterization of the tailing samples suggested that CV-0-B, CV-1, CV-5, and CV-10 contain phases that are difficult to digest. Since Zr is the element that differs between the different analyses, this might suggest a Zr dissolution problem in the mentioned samples. In other words, this can be interpreted as a presence of Zr, possibly in zircon, in samples CV-0-B, CV-1, CV-5, and CV-10. Although the dissolved tailing samples were visually inspected for signs of solid residues

(i.e. zircon), none were observed. No further tests for identifying zircon were done because determining the presence of zircon is beyond the scope of this research.

Due to the fact that CV-0-A was received first, the chemical characterization was first done for this sample. Later the rest of the tailing samples were received and subsequently their characterizations were done. It was expected that all the tailing samples would generally have similar mineral compositions. In addition, the quantity of CV-0-A sample received was considerably higher than the rest of the samples. Also, CV-0-A was never weathered (i.e., t=0), therefore, it gave an ideal starting composition of the mine tailing samples. For these reasons, CV-0-A was used in the optimization of the acid digestion method.

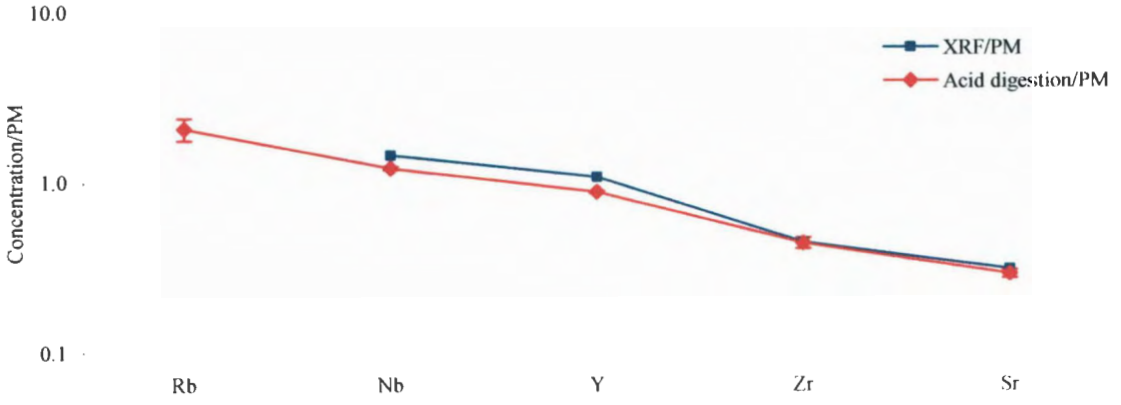


Figure 1. Comparison of analyses of CV-0-A by XRF and acid digestion.

Sample was analyzed once by XRF and six times by acid digestion. Rb concentration analyzed by XRF was below the L.D of the instrument.

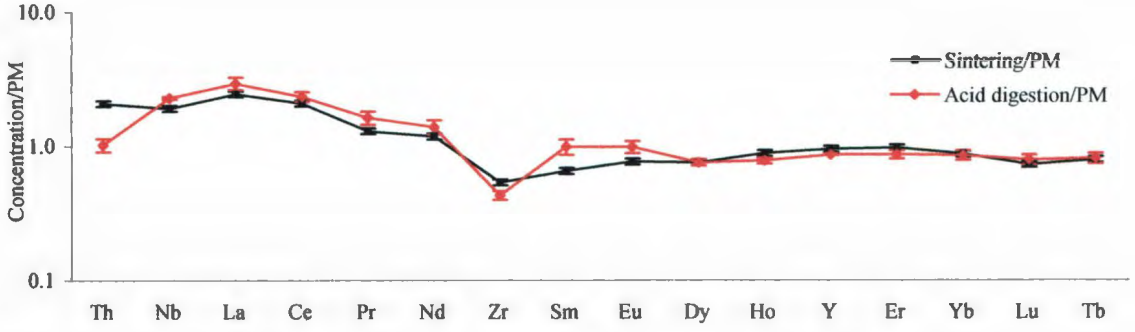


Figure 2. Comparison of analyses of CV-0-A by sintering and acid digestion.

Sample was analyzed once by sintering (has a 5% fixed r.s.d. error bars) and six times by acid digestion.

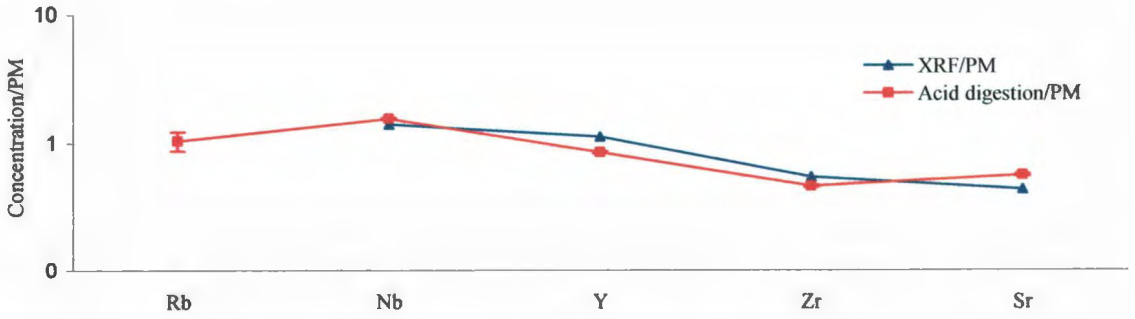


Figure 3. Comparison of analyses of CV-0-B by XRF and acid digestion.

Sample was analyzed once by XRF and four times by acid digestion. The Rb by XRF is <DL.

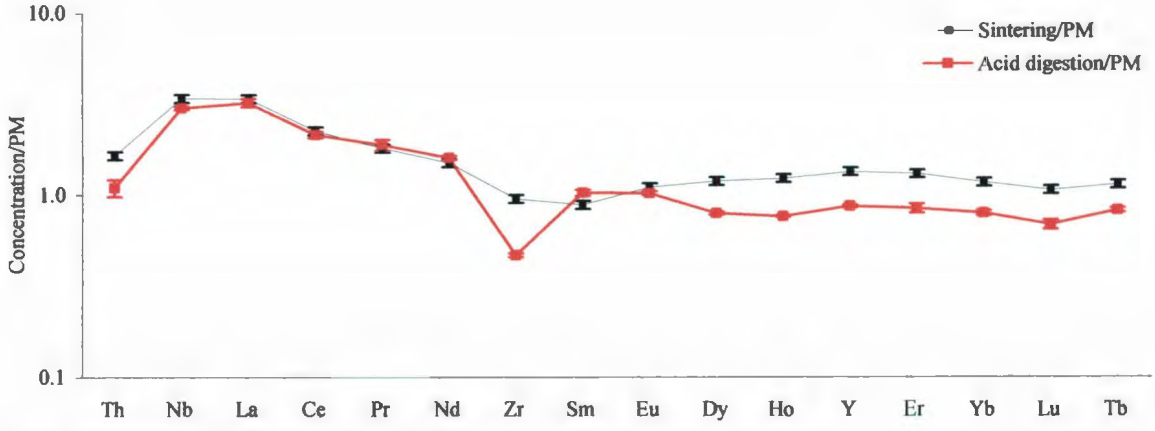


Figure 4. Comparison of analyses of CV-0-B by sintering and acid digestion.

Sample was analyzed once by sintering (has 5% fixed r.s.d. error bars) and four times by acid digestion.

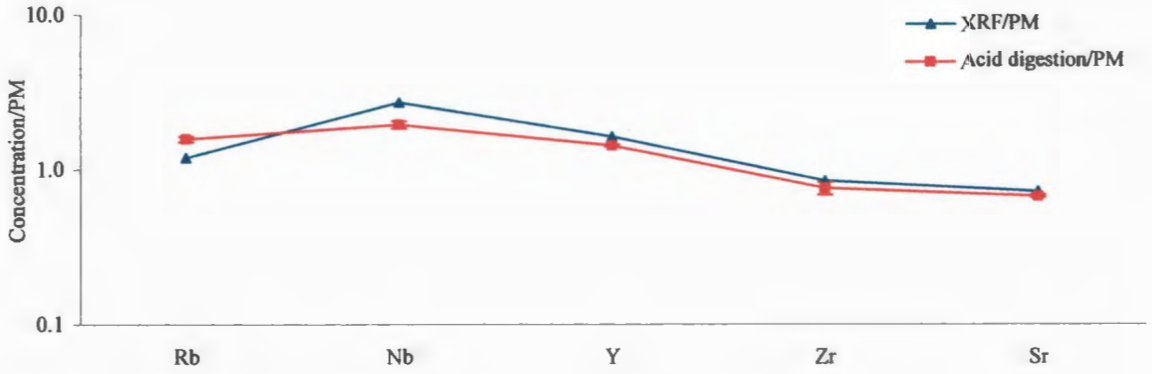


Figure 5. Comparison of analyses of CV-1 by XRF and acid digestion.

Sample was analyzed once by XRF and five times by acid digestion

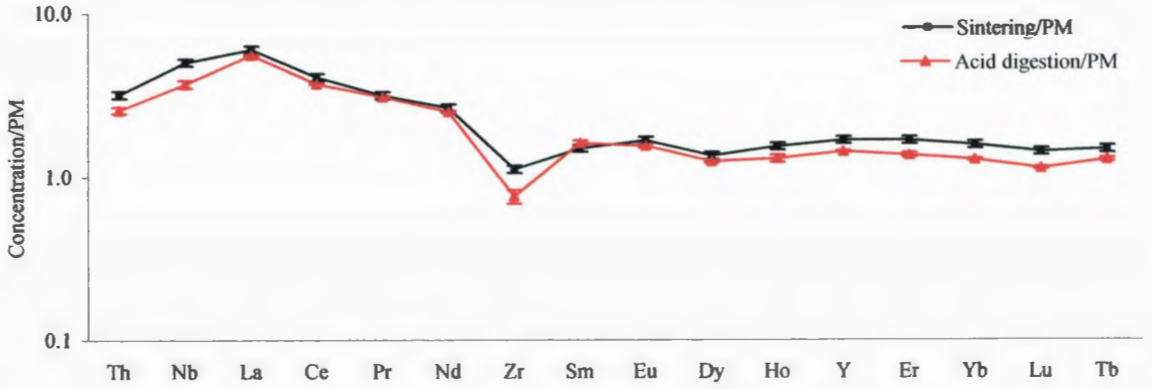


Figure 6. Comparison of analyses of CV-1 by sintering and acid digestion.

Sample was analyzed once by sintering (has a 5% fixed r.s.d. error bars) and five times by acid digestion.

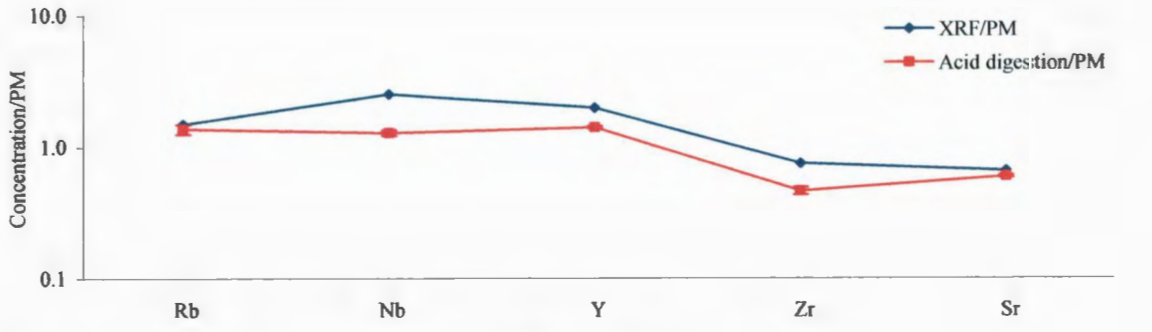


Figure 7. Comparison of analyses of CV-5 by XRF and acid digestion.

Sample was analyzed once by XRF and four times by acid digestion

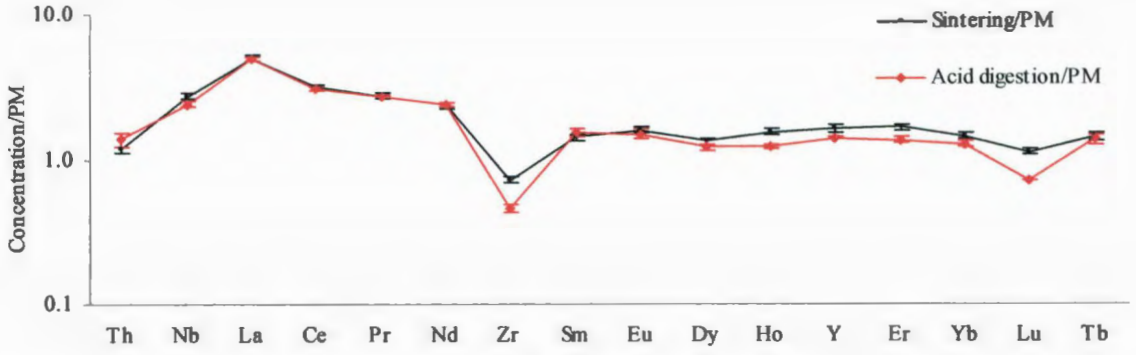


Figure 8. Comparison of analyses of CV-5 by sintering and acid digestion.

Sample was analyzed once by sintering (has 5% fixed r.s.d. error bars) and four times by acid digestion.

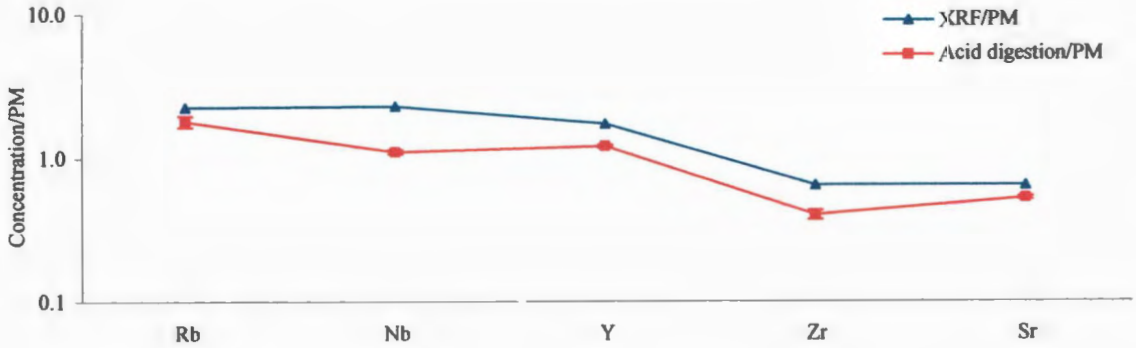


Figure 9. Comparison of analyses of CV-10 by XRF and acid digestion.

Sample was analyzed once by XRF and four times by acid digestion.

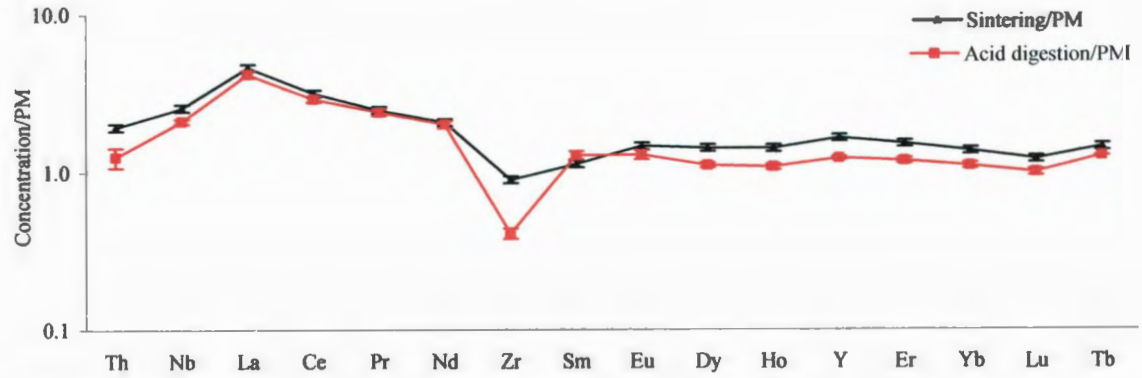


Figure 10. Comparison of analyses of CV-10 by sintering and acid digestion.

Sample was analyzed once by sintering (has 5% fixed r.s.d error bars) and four times by acid digestion.

3.3 Method Development of the Acid Digestion Procedure

The method development of the acid digestion procedure was focused on testing three variables of the original procedure. The variables tested were length of digestion, acid mixture, and stability of the resulting solution. The length of digestion experiments consisted of digesting samples from one to seven days to determine if digesting a sample more or less days would accomplish better recoveries. The acid mixture experiments consisted of a series of trials, where the amount and concentration of acids used in the original protocol were varied. These experiments intended to find an optimal acid mixture that would accomplish a complete digestion of the sample. The experiments on stability of the solution aimed to determine the most stable solution, which for the purpose of this research is defined as a solution that would maintain analytes in solution over time.

3.3.1 Length of Digestion

In the length of digestion experiments, the duration of digestion was varied in order to determine if a more optimal length for the digestion could be obtained. Samples of a reference material were digested from one to seven days in each cycle. The reference material selected was G-2 (Govindaraju, 1989), a granite which has been analyzed repeatedly at MUN using different methods, including a sintering digestion. This reference material was selected because when analyzed using the acid digestion protocol, it always showed low values for the HFSE due to the presence of difficult to digest refractory minerals. It was expected that increasing the length of digestion of the sample would show a consistent pattern of increasing recoveries for HFSE.

Table 5 presents the mean and standard deviation (of the mean results) for the length of digestion experiments (see Appendix 6 to review the complete data). The recoveries for HFSE did not show significant improvement when digesting the sample for a longer period of time. For example, the results for Zr were 39, 39, 36, 36, 43, 44, and 44 ppm for a length of digestion of one to seven days, respectively. These results are well below the recommended literature values of 309 ppm of Zr (Govindaraju, 1989) for G-2. These low recoveries indicated that undigested Zr-rich phases may be present. The results do not show the anticipated pattern of increasing HFSE recoveries with extended digestion times. Therefore, these results confirmed that the original length of digestion parameter was the optimal. Note that Table 5 also shows that recoveries for one-day digested-samples were consistently higher than recoveries of three-day digested-samples. Yet, the recoveries for HFSE are significantly below the recommended values. Also, the data do not show a clear pattern suggesting that a lesser length of digestion would increase HFSE recoveries. For example, day five, six, and seven, showed higher results for Zr than day three. For those reasons, the length of digestion was not further studied. However, more research could be done in the future regarding the higher recoveries observed for one-day digested samples. Note that the digested samples did not show visible precipitates. Therefore, samples were not filtered to determine the presence of hard to digest phases (i.e. zircon). Furthermore, determining these phases was beyond the scope of this research.

Table 5. Length of digestion experiments.

Element	L.D.	Recom. Values†		1 day**		2 days**		3 days**		4 days**		5 days**		6 days**		7 days**	
		ppm	±	$\bar{x}$	s($\bar{x}$)	$\bar{x}$	s($\bar{x}$)	$\bar{x}$	s($\bar{x}$)	$\bar{x}$	s($\bar{x}$)	$\bar{x}$	s($\bar{x}$)	$\bar{x}$	s($\bar{x}$)	$\bar{x}$	s($\bar{x}$)
Li	0.30	34	4	32	0.2	32	0.9	30	0.7	30	1.0	31	0.2	30	1	31	0.9
Rb	0.47	170	3	177	6.5	164	4.7	141	0.4	150	6.7	174	2.9	158	16	159	1.2
Sr	2.65	478	2	516	20	481	8	417	2	433	28	490	1	437	44	456	3
Y	0.25	11	2	8.7	0.4	8.0	0.4	7.0	0.0005	7.3	0.4	8.0	0.2	7.3	0.8	7.5	0.005
Zr	0.67	309	35	39	0.01	39	1	36	0.23	35	0	43	4	44	4	44	0.30
Nb	0.44	12		13.9	0.30	13.2	0.19	12.2	0.02	12.4	0.5	13.7	0.1	12.8	0.9	13.4	0.01
Mo	2.64			<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*	
Cs	0.17	1.34	0.16	1.5	0.05	1.5	0.02	1.4	0.05	1.3	0.03	1.4	0.02	1.3	0.1	1.3	0.02
Ba	1.64	1880	23	2503	80	2442	25	2232	33	2257	103	2461	35	2317	125	2436	37
La	0.14	89	8	92	2.2	89	0.7	82	0.7	83	3.5	90	1.3	85	4.2	89	1.3
Ce	0.14	160	10	178	5	166	2	150	2	153	8	166	2	156	8	156	3
Pr	0.12	18		17	0.2	17	0.4	16	0.3	16	0.7	17	0.2	16	0.7	17	0.4
Nd	1.86	55	12	56	1.6	53	1.0	49	0.5	50	2.7	54	0.7	50	2.7	52	1.1
Sm	0.91	7.2	0.7	8	0.2	7	0.04	7	0.1	7	0.2	7	0.02	6	0.4	7	0.1
Eu	0.32	1.4	0.12	1.5	0.01	1.4	0.03	1.3	0.03	1.2	0.07	1.3	0.01	1.2	0.07	1.2	0.016
Gd	0.63	4.3		3.2	0.10	2.9	0.13	2.8	0.07	2.7	0.13	2.7	0.01	2.6	0.11	3.0	0.048
Tb	0.12	0.48		0.4	0.003	0.4	0.01	0.3	0.01	0.3	0.01	0.3	0.002	0.3	0.01	0.3	0.001
Dy	0.51	2.4	0.3	2.2	0.02	2.1	0.03	1.8	0.03	1.9	0.07	1.8	0.01	1.8	0.12	1.7	0.068
Ho	0.11	0.4		0.4	0.004	0.3	0.001	0.3	0.01	0.3	0.01	0.3	0.01	0.2	0.01	0.2	0.001
Er	0.47	0.92		0.9	0.02	0.7	0.05	0.7	0.05	0.6	0.01	0.5	0.04	0.5	0.06	0.4	0.006
Tm	0.08	0.18		0.1	0.01	0.1	0.01	0.1	0.01	0.1	0.03	0.1	0.06	0.1	0.004	0.03	0.041
Yb	0.69	0.8	0.2	0.7	0.04	0.5	0.005	0.3	0.04	0.3	0.02	0.2	0.02	0.2	0.002	0.1	0.005
Lu	0.13	0.11		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*	
Hf	0.81	7.9	0.7	1.4	0.16	1.2	0.05	0.9	0.05	0.8	0.06	0.9	0.11	0.8	0.13	0.9	0.068
Ta	0.16	0.5		0.9	0.01	0.9	0.02	0.8	0.01	0.8	0.01	0.8	0.01	0.8	0.04	0.9	0.029
Tl	0.16			1.0	0.01	0.9	0.03	0.9	0.02	0.8	0.02	0.8	0.06	0.9	0.02	0.8	0.032
Pb	0.58	30	4	31	0.63	30	0.58	29	0.36	29	0.78	30	0.49	29	0.82	30	0.94
Bi	0.16	0.04		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*	0.01	<L.D.*	
Th	0.17	25	2	25	0.20	25	0.39	23	0.41	25	0.83	26	0.63	25	1.04	25	0.805
U	0.10			1.8	0.00	1.6	0.01	1.6	0.04	1.6	0.02	1.9	0.05	1.7	0.12	1.7	0.049

*Values below Limit of detection of the instrument, Recom. Values†: recommended values from Govindaraju (1989) ** Samples analyzed in duplicate (n=2)

3.3.2 Acid mixture

As mentioned in section 1.2.1, the acid digestion protocol uses several acids including HNO_3, HF, H_3BO_3, and $H_2C_2O_4$. These acids are added to the sample in order to accomplish a complete digestion and to maintain the analytes in solution. In this part of the study, several trials were carried out (T0–T10) and were done in triplicate to evaluate reproducibility. The composition of the acid mixture was changed in order to determine if a variation in the amounts or concentrations of the specific acids used would improve the acid digestion procedure. These trials were done in triplicate to evaluate reproducibility. The descriptions of the trials are described below.

3.3.3 First Set of Experiments

The first set of experiments compared the original digestion protocol with trials of modified versions of the original protocol. In this part of the study, nine different trials were carried out, using sample **CV-O-A**. In addition, the digested samples in these trials were diluted 10X and 20X (in the original protocol, the samples are diluted 20X). By diluting samples to 10X, the HFSE would be more concentrated and possibly would generate better results. The description of the trials is presented below.

- T0: Original procedure. The sample was digested according to the original procedure, previously described in the literature review. See the flow sheet in Appendix 1.
- T1: No H_3BO_3 acid. The sample was digested omitting the addition of H_3BO_3 after the second evaporation. Boric acid is used to complex remaining fluorides and may aid in the digestion of other components. With this alteration, it could be determined

if a precipitation (that could contain HFSE) occurred. See the flow sheet of the trial in Appendix 7.

- T2: Heating $H_2C_2O_4$+HF/H_3BO_3 mixture. In this trial, these acids were added after the last evaporation when the sample is in solution with nitric acid and is placed on the hot plate. This modification could allow an enhanced reaction of the sample, the $H_2C_2O_4$, and the HF/H_3BO_3 mix. See the flow sheet of the trial in Appendix 8.
- T3: 2 mL of HF. The sample was digested with 2 mL of HF (instead of 1mL of HF). This modification could increase the formation of fluorides and subsequently result in a better digestion of the sample. See the flow sheet of the trial in Appendix 9 .
- T4: No $H_2C_2O_4$ acid. The sample was digested omitting the addition of $H_2C_2O_4$. Oxalic acid is added to complex iron and aid in the digestion of other analytes. This test was conducted to determine if a precipitate was formed and if the analyte concentrations varied with respect to the analyte concentrations generated by the original procedure. See the flow sheet of the trial in Appendix 10.
- T5: No HF/H_3BO_3. The sample was made up to 60 g without adding the 0.665 mL of 0.113M HF/0.453M H_3BO_3 mixture. The test was carried out to determine if a precipitate was formed resulting in lower HFSE concentrations than the obtained using the original procedure. See the flow sheet of the trial in Appendix 11.
- T6: Different concentration of the HF/H_3BO_3 mixture (a). The concentration of the HF/ H_3BO_3 mixture was changed to determine if higher concentrations of HF would keep more HFSE in solution. The new acid concentration was 0.453 M HF/0.113 M

H_3BO_3 and 0.665 mL, was added. This concentration is closer to the stoichiometric reaction of the H_3BO_3 and the HF. See the flow sheet of the trial in Appendix 12.

- T7: Different concentration of the HF/H_3BO_3 mixture (b). As the previous test, the HF/H_3BO_3 mixture was changed to determine if higher concentrations of HF would keep more HFSE in solution. The modified concentration was 0.906M HF/0.113 M H_3BO_3 and 0.665 mL was added. See the flow sheet of the trial in Appendix 13.
- T8: Concentrated and non-distilled acids. The sample was digested according to the original procedure but the HNO_3 and HF were concentrated and were not distilled. Note that in the routine laboratory procedure, the acids are diluted before distillation, thus distilled acids are not as concentrated as stock concentrated acids.

The summary results of the trials T0 to T8, which includes the mean and standard deviation (of the mean), are shown in Tables 6 and 7. The complete set of data are shown in Appendices 14 to 18. The HFSE and the major elemental concentrations of the samples are plotted in Figures 11 to 13. Since less elements were plotted, it was not considered relevant to normalize these data to PM. Figures 11 to 13 do not show any improvement for the digestion of the HFSE using different procedures. In fact, the values obtained for the concentrations are almost identical. To further confirm these conclusions, a t-Test was done and the results are shown in Table 8 (see Appendix 3 to review the t-Test statistical concept). This test was selected due to the fact that it effectively assesses the means of two groups, determining if statistical significant differences exist between two means (Lomax, 2007). In this study, each trial was done in triplicate, which equals four degrees of freedom. The critical value or threshold for this test was 2.78, for a confidence level of 95%. Therefore, if the t-Test results generate

values larger than 2.78 then the means of the two groups compared are significantly different. Thus, smaller values than - 2.78, are considered statistically significant as well.

The t-Test verified that there was no statistical difference between any of the trials for the HFSE. However, there were significant statistical differences for Sr in trials T4, T5, and T7 as well as for Y in trials T2, T3 and T6. Although, trials T4 and T5 showed improvements for the analysis of Sr, these trials involved the elimination of the use of oxalic acid and the elimination of the use of HF/ H_3BO_3. The use of these acids is a key factor in the digestion of HFSE. Therefore, these trials were not considered for subsequent work. Note that T6 generated a t-Test value of -7.25, which means that the concentration of Y in T6 was considerably lower than the concentration of this element in T0. Since the objective of the study was to accomplish higher recoveries when digesting the samples, T6 was not further studied. Trials T2, T3, and T7 showed some improvements for the analyses of Sr and Y and the modifications in protocol would not interfere in the analyses of HFSE. Consequently, these trials were considered for the design of future experiments.

There were significant differences for other elements with other trials (Sm, Mo, Lu, Yb, etc. See Table 8). However, the concentrations of the mentioned elements were very close to the L.D. of the ICP-MS. Therefore, these statistical differences were not considered relevant for the subsequent experiments. The trails that were done using dilutions of 10X were not successful. This was due to the increase of the L.D. of the ICP-MS compared with the routine L.D. obtained in previous runs. In addition, in the Trial T2 (Heating $H_2C_2O_4$ + HF/ H_3BO_3 mixture) the formation of a precipitate (with possibly HFSE) was not observed.

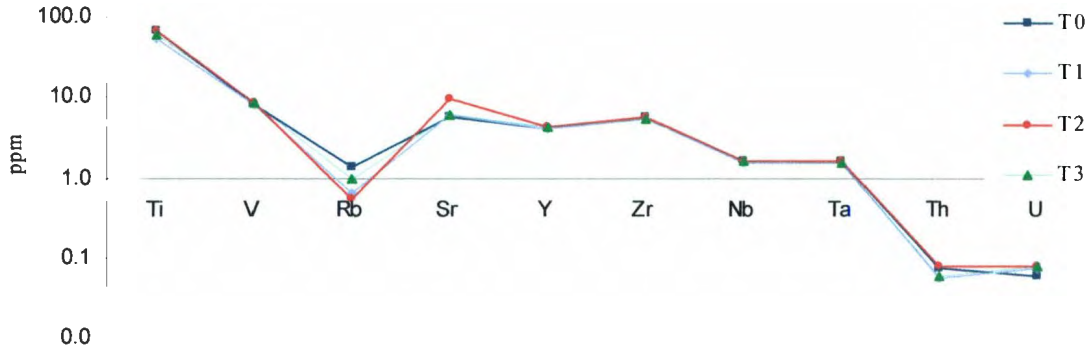


Figure 11. Trials T0 versus T1, T2, and T3.

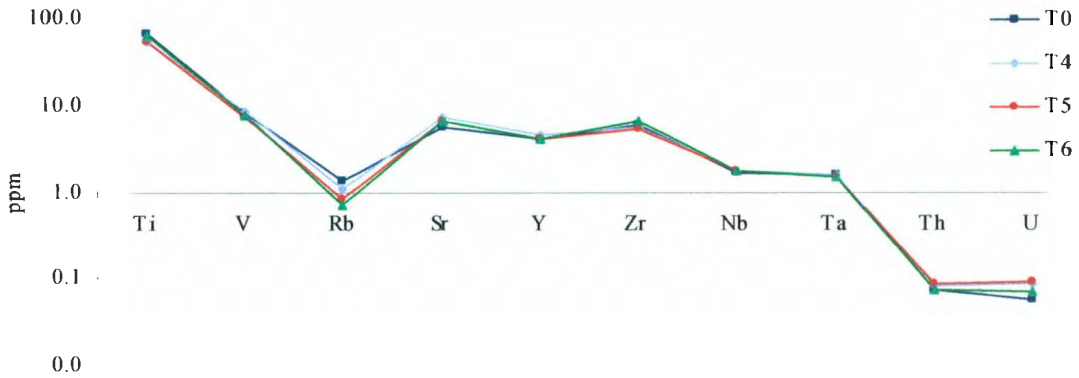


Figure 12. Trials T0 versus T4, T5, and T6.

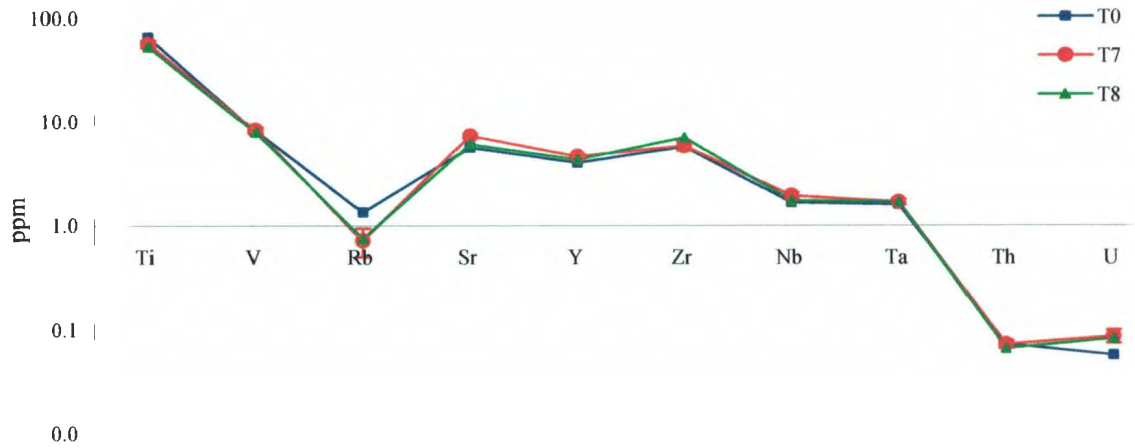


Figure 13. Trials T0 versus T7 and T8.

Table 6. First set of experiments (T0, T1, T2, T3, T4, T5, T6, T7 and T8).

	T0 (n=3)		T1 (n=3)		T2 (n=3)		T3 (n=2)		T4 (n=3)		T5 (n=3)		T6 (n=2)		T7 (n=3)		T8 (n=3)	
Element	$\bar{x}$	$s(\bar{x})$	$\bar{x}$	$s(\bar{x})$	$\bar{x}$	$s(\bar{x})$	$\bar{x}$	$s(\bar{x})$	$\bar{x}$	$s(\bar{x})$	$\bar{x}$	$s(\bar{x})$	$\bar{x}$	$s(\bar{x})$	$\bar{x}$	$s(\bar{x})$	$\bar{x}$	$s(\bar{x})$
Li	1.02	0.07	1.12	0.13	1.08	0.01	1.00	0.03	1.18	0.08	7.94	6.81	1.10	0.03	1.35	0.22	0.65	0.39
Ti	65	4.1	53	1.0	66	3.4	58	5.0	54.2	1.3	53	4.3	61	8.5	56	4.4	53	2.8
V	8.11	0.19	7.96	0.12	8.46	0.22	8.53	0.17	8.49	0.47	7.35	0.29	7.53	0.31	8.28	0.53	7.93	0.32
Cr	3.4	0.4	3.2	0.4	4.3	0.1	5.1	0.7	4.0	0.4	4.1	0.3	3.3	0.3	4.0	0.6	62	57
Rb	1.35	0.30	0.67	0.20	0.55	0.01	0.99	0.44	1.06	0.47	0.83	0.15	0.72	0.21	0.72	0.22	0.75	0.58
Sr	5.60	0.19	6.05	0.18	9.80	3.63	6.13	0.11	7.06	0.48	6.61	0.27	6.44	0.27	7.25	0.39	6.02	0.15
Y	3.99	0.03	4.13	0.09	4.25	0.07	4.25	0.01	4.54	0.24	4.04	0.15	4.08	0.12	4.61	0.27	4.28	0.21
Zr	5.69	0.36	5.36	0.24	5.68	0.14	5.44	0.11	5.59	0.44	5.32	0.37	6.35	0.25	5.78	0.61	6.99	1.40
Nb	1.65	0.08	1.57	0.02	1.61	0.02	1.67	0.02	1.74	0.12	1.72	0.06	1.73	0.07	1.94	0.14	1.73	0.09
Mo	0.37	0.11	0.35	0.10	0.63	0.01	0.54	0.10	0.92	0.22	1.15	0.09	0.83	0.10	1.08	0.13	0.82	0.12
Cs	0.38	0.02	0.19	0.01	0.43	0.05	0.40	0.02	0.33	0.02	0.24	0.01	0.21	0.01	0.21	0.02	0.06	0.06
Ba	8.41	1.40	8.74	0.39	22.46	8.77	8.92	0.40	9.38	0.63	9.44	0.78	8.20	0.75	7.86	0.73	9.74	0.63
La	1.81	0.12	2.10	0.24	2.12	0.19	1.80	0.002	2.14	0.17	2.05	0.16	1.84	0.06	2.02	0.02	1.97	0.13
Ce	3.79	0.26	4.09	0.27	4.12	0.21	3.75	0.02	4.13	0.23	3.94	0.23	3.96	0.11	4.21	0.10	3.99	0.23
Pr	0.38	0.02	0.47	0.03	0.49	0.04	0.41	0.02	0.49	0.02	0.47	0.03	0.44	0.01	0.48	0.01	0.47	0.04
Nd	1.53	0.03	1.86	0.14	1.97	0.13	1.66	0.04	2.20	0.19	2.08	0.12	1.96	0.06	2.13	0.12	1.95	0.18
Sm	0.27	0.03	0.40	0.03	0.42	0.02	0.40	0.003	0.55	0.09	0.64	0.04	0.50	0.01	0.62	0.08	0.46	0.08
Eu	0.13	0.01	0.15	0.01	0.18	0.01	0.17	0.004	0.20	0.02	0.22	0.01	0.14	0.01	0.23	0.01	0.16	0.01
Gd	0.49	0.03	0.55	0.03	0.59	0.01	0.57	0.009	0.68	0.06	0.64	0.03	0.49	0.01	0.65	0.04	0.54	0.01
Tb	0.07	0.004	0.07	0.003	0.08	0.003	0.08		0.10	0.01	0.10	0.005	0.09	0.004	0.10	0.01	0.08	0.003
Dy	0.51	0.01	0.52	0.02	0.58	0.01	0.55	0.0004	0.63	0.04	0.65	0.02	0.55	0.02	0.68	0.06	0.61	0.04
Ho	0.12	0.01	0.13	0.002	0.14	0.004	0.13	0.002	0.15	0.01	0.15	0.004	0.13	0.01	0.16	0.01	0.14	0.003
Er	0.36	0.02	0.41	0.01	0.44	0.005	0.43	0.0004	0.52	0.04	0.53	0.02	0.47	0.01	0.54	0.03	0.52	0.05
Tm	0.05	0.01	0.07	0.01	0.08	0.01	0.08	0.004	0.09	0.005	0.09	0.01	0.08	0.01	0.10	0.01	0.10	0.01
Yb	0.36	0.02	0.40	0.02	0.43	0.003	0.46	0.01	0.52	0.05	0.51	0.02	0.44	0.03	0.54	0.05	0.50	0.02
Lu	0.05	0.01	0.06	0.01	0.07	0.002	0.07	0.0004	0.08	0.01	0.09	0.004	0.07	0.001	0.09	0.01	0.06	0.01
Hf	< 0.11*		< 0.11*		< 0.11*		< 0.11*		0.16	0.07	0.20	0.01	<0.29*		<0.29*		0.04	0.02
Ta	1.59	0.03	1.58	0.01	1.66	0.03	1.54	0.06	1.60	0.07	1.47	0.05	1.50	0.04	1.69	0.10	1.68	0.10
Tl	<0.04*		<0.04*		<0.04*		<0.04*		<0.12*		<0.12*		<0.12*		<0.12*		<0.12*	
Pb	<1.89*		<1.89*		<1.89*		<1.89*		<0.40*		<0.40*		<0.40*		<0.40*		<0.40*	
Bi	<0.02*		<0.02*		<0.02*		<0.02*		<0.08*	0.005	<0.08*		<0.08*		<0.08*		<0.08*	
Th	0.07	0.01	0.06	0.01	0.08	0.01	0.06	0.001	0.08	0.02	0.09	0.01	0.07	0.01	0.07	0.01	0.07	0.006
U	0.06	0.003	0.07	0.01	0.08	0.004	0.08	0.003	0.09	0.002	0.09	0.01	0.07	0.01	0.09	0.01	0.08	0.014

Note that concentrations units are ppm. * Concentrations showing symbol < correspond to amounts below the L.D. of the instrument. It was not possible to determine several elemental concentrations (<L.D.); therefore, their correspondent $s(\bar{x})$ was not determined either.

Table 7. First set of experiments (using 10X dilution).

	T0-10X (n=3)		T1-10X (n=3)		T2-10X (n=3)		T3-10X (n=2)		T4-10X (n=3)		T5-10X (n=3)		T6-10X (n=2)		T7-10X (n=3)		T8-10X (n=3)	
Element	$\bar{x}$	$s(\bar{x})$	$\bar{x}$	$s(\bar{x})$	$\bar{x}$	$s(\bar{x})$	$\bar{x}$	$s(\bar{x})$	$\bar{x}$	$s(\bar{x})$	$\bar{x}$	$s(\bar{x})$	$\bar{x}$	$s(\bar{x})$	$\bar{x}$	$s(\bar{x})$	$\bar{x}$	$s(\bar{x})$
Li	0.72	0.05	1.33	0.09	1.38	0.07	0.51	0.38	0.99	0.15	1.54	0.23	1.96	0.16	1.76	0.54	0.02	0.72
Ti	62.5	7.45	46.1	3.47	56.6	1.70	60.2	12.1	46.9	1.40	46.5	3.61	57.9	9.08	51.2	1.56	54.8	0.63
V	8.19	0.08	6.92	0.36	7.22	0.13	7.20	0.07	7.41	0.08	6.64	0.14	7.60	0.31	7.56	0.09	8.04	0.24
Cr	1.44	0.70	49	3.49	58	1.54	69	4.20	104	7.2	106	4.3	183	16.5	140	1.5	192	17.3
Rb	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		0.03	0.78
Sr	3.66	0.56	6.43	0.13	9.87	3.71	5.60	0.23	5.31	0.11	5.57	0.14	5.62	0.12	5.85	0.13	6.48	0.11
Y	4.10	0.10	4.06	0.11	4.24	0.06	4.22	0.17	3.92	0.06	3.97	0.11	3.97	0.04	3.97	0.05	4.39	0.07
Zr	5.26	0.31	4.95	0.26	5.38	0.12	8.30	3.39	4.57	0.09	5.22	0.50	5.50	0.12	4.90	0.45	6.83	0.97
Nb	1.65	0.09	1.78	0.07	1.81	0.02	1.83	0.05	1.62	0.03	1.76	0.07	1.79	0.01	1.76	0.02	1.87	0.03
Mo	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		1.04	0.10
Cs	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		0.00	0.08
Ba	6.44	1.67	9.93	1.10	12.53	4.24	8.14	0.50	8.20	0.34	11.64	2.18	8.61	0.83	8.08	0.58	9.99	0.67
La	1.80	0.13	2.11	0.21	2.12	0.17	1.87	0.11	1.86	0.07	2.04	0.12	1.80	0.03	1.77	0.11	1.97	0.07
Ce	4.07	0.27	4.31	0.29	4.45	0.26	4.13	0.15	3.98	0.03	4.48	0.22	4.12	0.03	3.90	0.16	4.22	0.08
Pr	0.29	0.01	0.50	0.03	0.50	0.03	0.41	0.02	0.39	0.01	0.41	0.01	0.38	0.005	0.39	0.02	0.44	0.03
Nd	0.12	0.26	1.99	0.08	1.99	0.16	1.43	0.20	1.38	0.04	1.52	0.09	1.45	0.06	1.44	0.13	1.87	0.15
Sm	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		0.45	0.08
Eu	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		0.17	0.02
Gd	<L.D.*		0.55	0.03	0.55	0.02	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		0.56	0.04
Tb	<L.D.*		0.08	0.01	0.08		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		0.10	0.01
Dy	<L.D.*		0.60	0.03	0.61	0.01	0.53	0.06	0.48	0.01	0.47	0.03	0.46	0.01	0.50	0.01	0.61	0.04
Ho	<L.D.*		0.14	0.01	0.14	0.003	0.12	0.01	0.10	0.004	0.11	0.004	0.10	0.01	0.12	0.003	0.14	0.01
Er	<L.D.*	0.06	0.47	0.03	0.45	0.003	0.41	0.04	<L.D.*		0.36	0.003	0.36	0.02	0.37	0.01	0.46	0.05
Tm	<L.D.*		0.10	0.03	0.08	0.01	<L.D.*		<L.D.*		<L.D.*		<0.07		<L.D.*		0.09	0.02
Yb	<L.D.*		0.42	0.01	0.42	0.02	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		0.47	0.02
Lu	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		0.06	0.004
Hf	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		0.09	0.02
Ta	1.49	0.03	1.47	0.08	1.88	0.02	1.59	0.15	1.44	0.01	1.44	0.05	1.72	0.01	1.72	0.01	2.06	0.09
Tl	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<0.111		<L.D.*		0.04	0.02
Pb	<L.D.*		0.48	0.15	0.54	0.11	<L.D.*		0.36	0.06	<L.D.*		<L.D.*		<L.D.*		0.41	0.02
Bi	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		0.09	0.07
Th	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		0.06	0.01
U	<L.D.*		0.10	0.03	0.08	0.01	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		0.08	0.01

Note that concentrations units are ppm. * Concentrations showing symbol < correspond to amounts below the L.D. of the instrument. It was not possible to determine several elemental concentrations (<L.D.); therefore, their correspondent $s(\bar{x})$ was not determined either.

Table 8. t-Test for first set of experiments.

Element	T0-T1	T0-T2	T0-T3	T0-T4	T0-T5	T0-T6	T0-T7	T0-T8
Li	0.70	0.82	-0.29	1.51	1.02	0.64	1.45	-0.94
Ti	-2.99	0.05	-0.95	-2.56	-2.07	-1.13	-1.48	-2.53
V	-0.68	1.18	1.48	0.74	-2.19	-2.44	0.30	-0.49
Cr	-0.35	2.15	1.80	0.92	1.41	-0.52	0.73	1.02
Rb	-1.90	-0.07	-0.58	-0.52	-1.57	-1.98	-1.69	-0.91
Sr	1.73	1.16	2.30	2.85	3.08	1.91	3.77	1.72
Y	1.35	3.32	7.47	2.30	0.27	-7.25	2.29	1.32
Zr	-0.75	-0.02	-0.63	-0.16	-0.72	1.02	0.14	0.90
Nb	-1.02	-0.57	0.23	0.63	0.70	0.08	1.76	0.60
Mo	-0.11	2.34	1.00	2.21	5.62	0.39	4.21	2.71
Cs	-8.02	0.97	0.68	-1.71	-5.64	-7.27	-6.33	-5.39
Ba	0.22	1.58	0.34	0.63	0.64	0.27	-0.35	0.87
La	1.05	1.38	-0.11	1.54	1.16	-0.10	1.63	0.85
Ce	0.80	0.97	-0.17	1.00	0.45	0.21	1.51	0.57
Pr	2.39	2.61	1.03	3.96	2.39	2.35	4.75	2.18
Nd	2.33	3.33	2.19	3.48	4.26	5.49	5.05	2.31
Sm	3.22	4.18	3.82	3.05	6.92	6.63	4.28	2.25
Eu	0.99	3.05	2.70	2.68	6.37	0.95	5.55	-3.02
Gd	1.55	3.38	2.70	3.01	3.77	0.30	3.54	1.83
Tb	1.12	1.83	2.00	2.38	5.08	3.52	3.23	2.18
Dy	0.63	4.60	3.25	2.70	6.71	1.25	2.92	2.53
Ho	0.52	1.39	0.90	1.76	2.31	0.22	2.26	2.00
Er	2.58	4.64	4.73	3.44	6.12	4.33	5.54	3.06
Tm	1.58	2.43	2.80	5.20	3.88	3.09	3.90	3.50
Yb	1.60	3.47	4.51	2.84	6.03	2.38	3.68	5.28
Lu	0.82	3.05	3.83	3.14	5.79	2.89	3.41	1.47
Ta	-0.32	1.70	-0.57	0.21	-1.86	-2.40	0.96	0.87
Th	-1.09	0.27	-1.00	0.35	0.99	-0.23	-0.02	-0.45
U	2.42	4.05	4.41	8.26	2.92	1.46	2.25	1.77

Note that several elemental concentrations were <L.D and their t-Test value was not determined either.

3.3.4 Second Set of Experiments

The first set of experiments did not produce any clear trend in the data; however, Trials T2, T3, and T7 showed some improvements for the analyses of Sr and Y. For that reason, the three variables tested in these trials (extra heating step, amount of HF added, and concentration of HF/H_3BO_3) were considered in the second set of experiments. In these experiments, the mentioned variables were combined and evaluated. The new trials were done using sample **CV-0-A** and the reference materials **MESS-2**, **SY-2**, **AGV-1,** and **NIST-688**. MESS-2 is a marine sediment, SY-2 is a syenite, AGV is an andesite, and NIST-688 is a basalt (Govindaraju, 1989). Although these reference materials are neither

iron formations nor tailings, they were selected because they are known to have higher amounts of HFSE in their composition as compared to CV-0-A. Therefore, it should be possible to determine if the new trials produced a significant improvement when analyzing higher HFSE concentrations than in CV-0-A. These reference materials were also selected due to their availability and because they have been analyzed extensively by ICP-MS at MUN over the past 20 years. The new trials are described below:

- T9: This trial involved adding 0.665 mL of the 0.906M HF/0.113 M H_3BO_3 (instead of 0.665 mL of 0.113M HF/0.453M H_3BO_3). Then the sample in solution was heated. See the flow sheet of the trial in Appendix 19.
- T10: This trial involved the addition of 2 mL of HF (instead of 1 mL of HF). Also, it involved adding 0.665 mL of the 0.906M HF/0.113 M H_3BO_3 mixture. As in trial T9, the sample was heated after the addition of the acid mixture. See the flow sheet of the trial in Appendix 20.

It is important to note that the samples (CV-0-A, MESS-2, SY-2, AGV-1, NIST-688) were analyzed utilizing the new trials (T9 and T10) and the original procedure (T0). Then, the results of T9 and T10 were compared with the results of T0. The summary of these results is shown in Tables 9 to 13, while the complete set of results is given in Appendices 21 to 23. The results generated in T9 and T10 did not produce significant variations of the recoveries of HFSE. To further confirm these deductions, a t-Test was done and the results are shown in Table 14 (critical value was 2.78, 4 degrees of freedom, 95% confidence level).

One significant difference for the HFSE was detected in sample CV-0-A. The t-Test gave values of 4.8 for Zr and 5.9 for Ta. These results could suggest that there was

some improvement in the digestion of the sample when comparing trial T0 and T10. However, knowing that Zr and Hf are highly correlated, being almost always found together in minerals (as tetravalent elements with similar properties), it is expected to find a high t-Test value for Hf when the Zr t-value was also high. In the same way, Ta and Nb are generally found together in minerals (as pentavalent elements with similar properties). Therefore, it is expected to find a similar t-Test value for both elements. For these reasons, it was not considered that trials T9 and T10 produced significant improvements for HFSE recoveries. Consequently, it was considered not relevant to plot these trials.

Table 9. CV-0-A by trials T0, T9 and T10.

Element	T0 (n=3)		T9 (n=3)		T10 (n=3)	
	$\bar{x}$ (ppm)	s ($\bar{x}$)	$\bar{x}$ (ppm)	s ($\bar{x}$)	$\bar{x}$ (ppm)	s ($\bar{x}$)
Li	17.1	8.52	<L.D.*		<L.D.*	
Ti	55.2	7.20	52.0	6.02	53.7	1.98
V	7.24	0.25	6.90	0.12	7.55	0.31
Cr	1610	136	1500	249	2000	112
Rb	<L.D.*		<L.D.*		<2.16	
Sr	4.94	0.18	5.61	0.65	4.65	0.34
Y	3.74	0.01	3.97	0.05	3.85	0.06
Zr	4.63	0.15	4.80	0.25	5.78	0.18
Nb	1.54	0.10	1.60	0.09	1.60	0.05
Mo	<L.D.*		<L.D.*		<L.D.*	
Cs	<L.D.*		<L.D.*		<L.D.*	
Ba	7.70	0.33	7.44	0.50	7.74	0.41
La	2.25	0.20	2.28	0.29	1.79	0.05
Ce	3.96	0.14	4.26	0.38	3.62	0.10
Pr	0.48	0.01	0.46	0.04	0.41	0.02
Nd	1.58	0.07	1.63	0.12	1.27	0.09
Sm	0.55		<L.D.*		<L.D.*	
Eu	0.15	0.01	0.18	0.01	<L.D.*	
Gd	0.30	0.02	<L.D.*		<L.D.*	
Tb	<L.D.*		<L.D.*		<L.D.*	
Dy	0.53	0.03	0.55	0.05	0.47	0.02
Ho	0.11	0.01	0.12	0.01	0.10	0.01
Er	0.35	0.01	0.37	0.03	0.32	0.04
Tm	0.08	0.01	0.08		<L.D.*	
Yb	<L.D.*		0.35	0.03	<L.D.*	
Lu	<L.D.*		<L.D.*		<L.D.*	
Hf	<L.D.*		<L.D.*		<L.D.*	
Ta	7.04	0.33	6.95	0.87	9.51	0.25
Tl	<L.D.*		<L.D.*		<L.D.*	
Pb	<L.D.*		<L.D.*		<L.D.*	
Bi	<L.D.*		<L.D.*		<L.D.*	
Th	<0.05		<L.D.*		<L.D.*	
U	0.05	0.01	<L.D.*		<L.D.*	

* Concentrations below L.D. of the instrument. For those concentrations, the s($\bar{x}$) was not determined (blank spaces).

Table 10. NIST -688 by trials T0, T9 and T10.

Element	T0 (n=3)		T9 (n=3)		T10 (n=3)	
	$\bar{x}$ (ppm)	s ($\bar{x}$)	$\bar{x}$ (ppm)	s ($\bar{x}$)	$\bar{x}$ (ppm)	s ($\bar{x}$)
Li	9 58	0.16	11.43	1 25	10 01	0 55
Ti	6403	211	6468	208	6389	56
V	234	4 85	233	5 89	231	2 26
Cr	1268	23 6	1372	60 0	1388	19 8
Rb	2 04	0 31	2 07	0 37	1 91	0 28
Sr	147	3 23	146	3 05	148	2 22
Y	16	0 21	16 4	0 24	16 3	0 28
Zr	51	1 16	50 2	0 78	49 3	1 11
Nb	< L.D *		< L.D *		< L.D *	
Mo	< L.D *		< L.D *		< L.D *	
Cs	< L.D *		< L.D *		< L.D *	
Ba	153	1 05	151	0 78	155	4 40
La	5 11	0 06	5 02	0 04	5 17	0 11
Ce	10 9	0 10	10 4	0 16	10 9	0 27
Pr	1 72	0 03	1 67	0 01	1 73	0 04
Nd	7 55	0 11	7 60	0 09	7 61	0 16
Sm	2 18	0 07	2 12	0 01	2 29	0 04
Eu	0 90	0 03	0 90	0 02	0 94	0 03
Gd	1 99	0 03	2 01	0 03	2 03	0 02
Tb	0 41	0 01	0 39	0 004	0 42	0 01
Dy	3 20	0 02	3 07	0 03	3 15	0 05
Ho	0 68	0 01	0 66	0 004	0 67	0 01
Er	1 96	0 02	1 89	0 02	1 99	0 03
Tm	0 31	0 01	0 30	0 01	0 32	0 01
Yb	1 88	0 03	1 87	0 04	1 90	0 002
Lu	0 29	0 01	0 29	0 01	0 29	0 004
Hf	1 41	0 03	1 42	0 03	1 43	0 04
Ta	0 22	0 01	0 24	0 01	0 25	0 01
Tl	< L.D *		< L.D *		< L.D *	
Pb	2 73	0 44	2 97	0 56	2 66	0 17
Bi	< L.D *		< L.D *		< L.D *	
Th	0 34	0 02	0 33	0 01	0 34	0 01
U	0 27	0 02	0 32	0 08	0 26	0 01

Table 11. MESS-2 by trials T0, T9 and T10.

Element	T0 (n=3)		T9 (n=3)		T10 (n=3)	
	$\bar{x}$ (ppm)	s ($\bar{x}$)	$\bar{x}$ (ppm)	s ($\bar{x}$)	$\bar{x}$ (ppm)	s ($\bar{x}$)
Li	9 58	0 16	11 43	1 25	10 01	0 55
Ti	6403	211	6468	208	6389	56
V	234	4 85	233	5 89	231	2 26
Cr	1268	23 6	1372	60 0	1388	19 8
Rb	2 04	0 31	2 07	0 37	1 91	0 28
Sr	147	3 23	146	3 05	148	2 22
Y	16	0 21	16 4	0 24	16 3	0 28
Zr	51	1 16	50 2	0 78	49 3	1 11
Nb	< 0 32		< 0 32		< 0 32	
Mo	< 1 62		< 1 62		< 1 62	
Cs	< 0 19		< 0 19		< 0 19	
Ba	153	1 05	151	0 78	155	4 40
La	5 11	0 06	5 02	0 04	5 17	0 11
Ce	10 9	0 10	10 4	0 16	10 9	0 27
Pr	1 72	0 03	1 67	0 01	1 73	0 04
Nd	7 55	0 11	7 60	0 09	7 61	0 16
Sm	2 18	0 07	2 12	0 01	2 29	0 04
Eu	0 90	0 03	0 90	0 02	0 94	0 03
Gd	1 99	0 03	2 01	0 03	2 03	0 02
Tb	0 41	0 01	0 39	0 004	0 42	0 01
Dy	3 20	0 02	3 07	0 03	3 15	0 05
Ho	0 68	0 01	0 66	0 004	0 67	0 01
Er	1 96	0 02	1 89	0 02	1 99	0 03
Tm	0 31	0 01	0 30	0 01	0 32	0 01
Yb	1 88	0 03	1 87	0 04	1 90	0 002
Lu	0 29	0 01	0 29	0 01	0 29	0 004
Hf	1 41	0 03	1 42	0 03	1 43	0 04
Ta	0 22	0 01	0 24	0 01	0 25	0 01
Tl	< 0 1		< 0 1		< 0 1	
Pb	2 73	0 44	2 97	0 56	2 66	0 17
Bi	< 0 11		< 0 11		< 0 11	
Th	0 34	0 02	0 33	0 01	0 34	0 01
U	0 27	0 02	0 32	0 08	0 26	0 01

* Concentrations below L.D. of the instrument. The s($\bar{x}$) was not determined for elements <L.D (blank spaces).

Table 12. AGV-1 by trials T0, T9 and T10.

Element	T0 (n=3)		T9 (n=3)		T10 (n=3)	
	$\bar{x}$ (ppm)	s ($\bar{x}$)	$\bar{x}$ (ppm)	s ($\bar{x}$)	$\bar{x}$ (ppm)	s ($\bar{x}$)
Li	21.6	1.76	18.6	0.61	16.8	0.49
Ti	6900	418	6456	344	6222	161
V	135	8.11	124	7.24	120	3.40
Cr	476	30.5	476	34.7	442	21.7
Rb	61.5	11.09	60.23	1.19	61.97	0.82
Sr	614	64.8	577	7.02	590	6.43
Y	19.5	1.36	18.1	0.55	17.7	0.13
Zr	228	15.1	212	6.21	206	0.98
Nb	17.8	1.32	16.2	0.48	15.6	0.10
Mo	5.43	0.72	3.83	0.27	<L.D.*	
Cs	2.20	0.22	1.84	0.07	1.70	0.01
Ba	1593	128	1484	33.6	1434	15.3
La	37.2	4.51	35.8	0.47	36.0	0.32
Ce	64.7	6.21	61.4	0.94	60.5	0.76
Pr	8.37	1.00	7.95	0.13	7.94	0.05
Nd	31.8	3.75	28.7	0.49	28.5	0.09
Sm	6.78	0.86	5.66	0.16	5.33	0.10
Eu	1.99	0.23	1.65	0.08	1.52	0.03
Gd	2.44	0.27	1.83	0.12	1.86	0.07
Tb	0.50	0.06	0.40	0.02	0.34	0.01
Dy	4.14	0.43	3.45	0.12	3.23	0.04
Ho	0.81	0.10	0.65	0.03	0.58	0.01
Er	2.54	0.41	1.83	0.10	1.60	0.06
Tm	0.42	0.06	0.30	0.02	0.25	0.01
Yb	2.46	0.26	1.69	0.12	1.34	0.03
Lu	0.42	0.06	0.27	0.02	<L.D.*	
Hf	6.21	0.64	5.13	0.16	4.69	0.07
Ta	1.04	0.12	0.81	0.05	0.73	0.01
Tl	0.81	0.12	0.61	0.05	0.49	0.03
Pb	36.40	3.10	32.82	0.47	32.40	0.78
Bi	<L.D.*		<L.D.*		<L.D.*	
Th	6.52	0.71	6.02	0.03	5.88	0.02
U	1.99	0.23	1.71	0.03	1.65	0.02

Table 13. SY-2 by trials T0, T9 and T10.

Element	T0 (n=3)		T9 (n=3)		T10 (n=3)	
	$\bar{x}$	s ($\bar{x}$)	$\bar{x}$	s ($\bar{x}$)	$\bar{x}$	s ($\bar{x}$)
Li	95.9	2.89	92.9	1.64	85.9	1.61
Ti	868	29.0	819	27.3	778	6.45
V	53.8	1.74	49.9	1.92	47.9	0.71
Cr	400	14.5	349	18.0	325	5.16
Rb	209	8.45	206	2.13	199	2.78
Sr	252	8.80	252	3.28	244	4.16
Y	112	4.40	112	0.89	109	1.56
Zr	267	9.40	271	2.83	264	6.80
Nb	34.3	1.38	34.5	0.26	33.1	0.56
Mo	<L.D.*		<L.D.*		<L.D.*	
Cs	2.80	0.10	2.78	0.06	2.62	0.06
Ba	412	16.2	408	6.03	396	7.63
La	68.1	2.33	67.6	1.33	65.2	0.61
Ce	147	5.34	149	3.62	144	2.24
Pr	19.6	0.62	19.4	0.30	18.8	0.20
Nd	72.2	2.85	72.1	1.57	69.2	1.00
Sm	16.1	0.47	15.4	0.34	15.1	0.24
Eu	2.70	0.10	2.57	0.05	2.44	0.07
Gd	10.4	0.57	9.90	0.14	9.80	0.20
Tb	2.28	0.09	2.26	0.05	2.16	0.05
Dy	19.2	0.76	19.0	0.36	18.4	0.34
Ho	4.41	0.17	4.37	0.09	4.22	0.08
Er	14.3	0.56	14.2	0.28	13.70	0.23
Tm	2.40	0.10	2.37	0.03	2.28	0.01
Yb	16.8	0.55	16.6	0.31	16.2	0.34
Lu	2.86	0.10	2.77	0.05	2.70	0.04
Hf	8.39	0.25	8.06	0.17	7.88	0.24
Ta	1.81	0.07	1.76	0.04	1.70	0.02
Tl	2.77	0.08	2.59	0.04	2.44	0.03
Pb	85.1	2.78	84.0	1.39	81.2	1.01
Bi	<L.D.*		<L.D.*		<L.D.*	
Th	364	11.81	355	3.22	353	5.19
U	252	11.79	252	4.62	237	9.65

* Concentrations below L.D. of the instrument. Ffor those elements, the s($\bar{x}$) was not determined (blank spaces).

Table 14. t-Test for the second set of experiments.

Element	AVG-1		NIST 688		CV-0-A		SY-2		Mess-2	
	T0-T1	T0-T2	T0-T1	T0-T2	T0-T1	T0-T2	T0-T1	T0-T2	T0-T1	T0-T2
Ti	-0.82	-1.51	0.22	-0.07	-0.34	-0.2	-1.26	-3.06	4.11	2.12
V	-1.01	-1.68	-0.16	-0.53	-1.23	0.77	-1.51	-3.12	3.39	2.06
Cr	-1.01	-0.34	-0.83	-0.9	0.22	-0.39	-0.36	0.11	2.06	1.69
Cr	0.01	-0.92	1.6	3.88	-0.43	2.15	-2.23	-4.89	1.05	0.91
Rb	-0.11	0.05	0.06	-0.31			-0.33	-1.08	1.64	0.53
Sr	-0.57	-0.37	-0.35	0.09	0.99	-0.75	0	-0.79	1.23	0.48
Y	-0.99	-1.37	-0.14	-0.32	4.73	1.81	0.1	-0.59	2.65	3.92
Zr	-1	-1.47	-0.4	-0.94	0.6	4.82	0.4	-0.29	2.23	1.37
Nb	-1.14	-1.67	-0.32	0.07	0.44	0.52	0.14	-0.78	2.11	0.44
Mo	-2.36	-3.6	2.26	2.32			-4.06	-2.98	0.69	0.41
Cs	-1.6	-2.32	1.6	0.96			-0.13	-1.5	2.67	2.84
Ba	-0.83	-1.23	-1.05	0.44	-0.44	0.07	-0.22	-0.9	2.51	1.98
La	-0.31	-0.26	-1.32	0.46	0.1	-2.23	-0.16	-1.18	1.34	2.24
Ce	-0.52	-0.67	-2.67	0.01	0.75	-1.98	0.2	-0.65	1.85	3.12
Pr	-0.42	-0.44	-1.46	0.26	1.79	-2.97	-0.36	-1.17	1.01	2.31
Nd	-0.84	-0.9	0.31	0.28	0.31	-0.31	-0.01	-0.99	1.05	2.47
Sm	-1.28	-1.68	-0.83	1.45			-1.21	-1.88	1.48	3.19
Eu	-1.4	-2.07	-0.1	0.95			-1.13	-2.13	5.48	5.23
Gd	-2.1	-2.13	0.64	1.23			-0.84	-0.99	-0.61	1.23
Tb	-1.6	-2.6	-1.17	0.71			-0.26	-1.23	0.48	6.74
Dy	-1.53	-2.09	-3.58	-1.09	0.4	-1.71	-0.26	-0.89	6.21	6.79
Ho	-1.56	-2.29	-2.1	-0.68	0.68	-0.01	-0.2	-1.04	3.82	5.93
Er	-1.68	-2.25	-2.45	0.66	0.57	-0.69	-0.1	-1	-21.71	-21.41
Tm	-1.92	-2.85	-0.28	0.89	-0.97	-0.73	-0.37	-1.28	2.72	4.63
Yb	-1.6	-4.29	-0.12	0.52	0.91	-1.58	-0.25	-0.89	1.28	3.51
Lu	-2.54	-3.62	0.08	0.94			-0.82	-1.56	3.87	7.52
Hf	-1.64	-2.37	0.25	0.6			-1.06	-1.44	0.74	1.16
Ta	-1.72	-2.47	0.66	1.7	-0.1	5.94	-0.64	-1.6	1.62	1.58
Tl	-1.6	-2.7					-1.94	-3.63	3.81	1.48
Pb	-1.14	-1.25	0.34	-0.16			-0.35	-1.3	1.6	-1.25
Bi	-1.94	-2.91							0.8	0.85
Th	-0.9	-2.57	-0.25	-0.02	-0.14	-0.3	-0.67	-0.79	2.06	2.62
U	-1.2	-1.47	0.6	-0.4			-0.03	-0.99	1.93	3.87

Note that several elemental concentrations were <L.D. and their t-Test was not determined (blank spaces).

3.3.5 Third Set of Experiments

Based on over 20 years of experience with a wide range of samples, the Earth Sciences department at MUN recommends analyzing samples using ICP-MS as soon as possible after digestion. This recommendation, however, is not always practical since situations or delays may arise and the sample may not be analyzed immediately. For this reason, there is a need for methods which produce more stable solutions (analytes are maintained in solution over time).

As mentioned in section 3.3.4, trials T0, T9, and T10 did not show any significant improvement in the recoveries for HFSE (although the t-Test values for Zr and Ta were high). It was necessary, however, to determine if the solutions generated using trials T9 or T10 would maintain more analytes in solution over time than the solution generated

using trial T0. The third set of experiments involved digesting all the tailing samples using the mentioned trials. The solutions generated were analyzed, stored for two months, and re-analyzed (after 2 months). The results generated from both set of analyses were compared to determine the procedure which optimized the stability of the stored solutions. The most stable solution would be the one in which the concentrations decrease the least with storage.

Table 15 shows the mean and standard deviation (of the mean) from trials T0, T9 and T10 for the tailing samples. Table 16 shows the mean results of the same trials but analysed two months after digestion. The complete set of analyses are shown in Appendix 24 and 25. The results shown in Table 16 illustrate that the majority of the elements are below the limit of detection of the ICP-MS. For that reason, the standard deviation (of the mean) was not calculated in Table 16. Due to the fact that the majority of elemental concentrations in Table 16 were below the limit of detection of the ICP-MS, no quantitative comparison could be made in order to determine the most stable protocol. It was concluded that none of the solutions were stable two months after digestion and samples should be analyzed soon after digestion, which reinforces the recommendation of the Earth Sciences Department. Future research could determine the length of time that a solution remains stable (re-analyzing samples after a week, two weeks, etc).

Three sets of experiments were done during this study, in which the length of digestion, acid mixture, and stability of the solution were tested. None of these experiments showed improvements in the recovery for HFSE, which confirm that the original parameters of the protocol were the most optimal. For that reason, the original protocol was used to determine the environmental mobility in tailing samples.

Table 15. CV-0-A, CV-0-B, CV-1, CV-5 & CV-10.

	CV-0-A						CV-0-B						CV-1					
	T0 (n=3)		T9 (n=3)		T10 (n=3)		T0 (n=3)		T9 (n=3)		T10 (n=3)		T0 (n=3)		T9 (n=3)		T10 (n=3)	
Element	$\bar{x}$	s ($\bar{x}$)	$\bar{x}$	s ($\bar{x}$)	$\bar{x}$	s ($\bar{x}$)	$\bar{x}$	s ($\bar{x}$)	$\bar{x}$	s ($\bar{x}$)	$\bar{x}$	s ($\bar{x}$)	$\bar{x}$	s ($\bar{x}$)	$\bar{x}$	s ($\bar{x}$)	$\bar{x}$	s ($\bar{x}$)
Li	1.18	0.07	1.12	0.05	1.14	0.08	1.45	0.43	1.02	0.07	1.74	0.67	1.25	0.06	1.20	0.05	1.41	0.10
Ti	49.1	2.5	46.7	4.1	49.9	1.24	73.8	1.0	75.0	1.6	69.9	1.05	199	3	194	5.0	187	6.75
V	6.84	0.17	6.49	0.22	8.00	0.11	10.5	0.1	10.3	0.03	9.40	0.26	19.1	0.2	18.3	0.3	18.1	0.43
Cr	62.2	3.9	54.5	1.8	63.6	0.33	335	3.2	332	2.8	277	2.67	442	4	437	2.78	432	3.41
Rb	0.88	0.19	0.73	0.24	0.67	0.14	0.74	0.18	0.72	0.10	0.98	0.28	1.07	0.15	1.15	0.23	1.32	0.30
Sr	8.60	1.67	6.84	0.30	6.54	0.14	13.2	3.98	8.92	0.12	8.79	0.19	14.4	0.5	14.3	0.3	14.1	0.03
Y	4.07	0.12	4.06	0.14	4.34	0.03	4.00	0.09	3.81	0.07	3.54	0.08	6.64	0.12	6.37	0.09	6.44	0.03
Zr	4.22	0.08	4.50	0.14	6.09	0.55	5.32	0.15	5.83	0.33	6.11	0.97	7.33	0.70	6.60	0.15	6.66	0.18
Nb	1.66	0.04	1.81	0.19	1.78	0.05	2.21	0.05	2.16	0.04	2.07	0.03	2.88	0.06	2.70	0.08	2.70	0.06
Mo	1.88	0.41	3.31	1.53	1.76	0.61	3.68	0.35	4.81	0.10	4.14	0.44	5.01	0.69	5.25	0.75	4.46	0.14
Cs	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*	
Ba	11.6	3.27	8.91	0.20	9.06	0.45	14.1	0.5	12.5	0.7	11.9	0.52	18.5	0.4	18.6	0.3	19.2	0.54
La	2.28	0.40	1.88	0.06	2.13	0.25	2.17	0.13	2.08	0.09	1.86	0.01	3.91	0.02	3.93	0.04	4.16	0.13
Ce	4.68	0.60	4.09	0.08	4.37	0.32	3.74	0.17	3.53	0.09	3.14	0.05	6.71	0.04	6.72	0.05	7.22	0.20
Pr	0.54	0.08	0.45	0.01	0.48	0.02	0.51	0.04	0.49	0.02	0.45	0.01	0.86	0.01	0.86	0.03	0.87	0.01
Nd	2.30	0.33	1.84	0.03	1.95	0.14	2.12	0.06	1.97	0.10	2.02	0.09	3.45	0.10	3.38	0.08	3.44	0.03
Sm	0.58	0.07	0.48	0.01	0.48	0.03	0.45	0.02	0.45	0.06	0.57	0.02	0.73	0.05	0.69	0.07	0.67	0.04
Eu	0.21	0.01	0.17	0.01	0.17	0.01	0.17	0.005	0.17	0.002	0.18	0.01	0.27	0.01	0.26	0.01	0.25	0.002
Gd	0.57	0.02	0.52	0.01	0.55	0.03	0.52	0.01	0.56	0.05	0.52	0.01	0.81	0.01	0.85	0.03	0.81	0.01
Tb	0.10	0.003	0.09	0.003	0.09	0.002	0.08	0.003	0.08	0.003	<L.D.*		0.13	0.005	0.12	0.003	0.12	0.001
Dy	0.63	0.03	0.61	0.02	0.63	0.02	0.59	0.01	0.55	0.01	0.54	0.01	0.93	0.03	0.90	0.02	0.89	0.01
Ho	0.14	0.001	0.14	0.01	0.14	0.004	0.13	0.002	0.12	0.002	0.12	0.003	0.20	0.004	0.20	0.002	0.19	0.003
Er	0.49	0.01	0.48	0.01	0.45	0.02	0.41	0.03	0.39	0.01	0.39	0.01	0.66	0.04	0.62	0.02	0.63	0.01
Tm	0.09	0.01	0.09	0.01	0.09	0.01	0.08	0.01	0.08	0.01	<L.D.*		0.11	0.02	0.11	0.02	0.10	0.01
Yb	0.51	0.02	0.46	0.02	0.45	0.01	0.40	0.01	0.38	0.01	0.41	0.02	0.63	0.01	0.60	0.03	0.60	0.03
Lu	0.07	0.003	0.06	0.003	0.06	0.002	0.05	0.004	0.05	0.000	0.05	0.004	0.09	0.001	0.08	0.004	0.08	0.003
Hf	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*	
Ta	1.60	0.02	1.52	0.03	1.54	0.02	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*	
Tl	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*	
Pb	0.86	0.37	0.92	0.50	0.97	0.51	0.65	0.06	0.51	0.02	<L.D.*		0.62	0.08	0.50	0.02	0.72	0.17
Bi	<L.D.*		0.09	0.03	0.16	0.08	0.10	0.01	0.11	0.02	<L.D.*		<L.D.*		0.10	0.02	<L.D.*	
Th	0.10	0.01	0.09	0.02	$\tilde{x}$.08	0.01	0.09	0.01	0.08	0.005	0.10	0.01	0.20	0.001	0.21	0.002	0.22	0.01
U	0.09	0.01	0.08	0.01	0.08	0.01	<L.D.*		<L.D.*		<L.D.*		0.08	0.003	0.07	0.01	0.06	0.001

* Concentrations below L.D. of the instrument. Note that it was not possible to determine several elemental concentrations (<L.D.); for those elements, the s($\bar{x}$) was not determined either. All the elemental concentrations are in ppm.

Table 15. CV-0-A, CV-0-B, CV-1, CV-5 & CV-10.

	CV-5						CV-10					
	T0 (n=3)		T9 (n=3)		T10 (n=3)		T0 (n=3)		T9 (n=3)		T10 (n=3)	
Element	$\bar{x}$	s ($\bar{x}$)	$\bar{x}$	s ($\bar{x}$)	$\bar{x}$	s ($\bar{x}$)	$\bar{x}$	s ($\bar{x}$)	$\bar{x}$	s ($\bar{x}$)	$\bar{x}$	s ($\bar{x}$)
Li	0.87	0.12	0.74	0.09	0.76	0.14	1.02	0.12	1.19	0.23	1.27	0.14
Ti	195	7	204	18	199	10.7	127	8	123	6	152	1.76
V	16.5	0.9	17.0	0.5	17.4	0.48	12.2	0.9	11.2	0.3	15.3	0.30
Cr	279	6	275	5	276	13.1	267	23	212	3	313	24
Rb	1.06	0.24	1.21	0.13	1.28	0.35	1.15	0.15	1.21	0.14	1.23	0.24
Sr	12.2	0.3	11.3	0.05	11.5	0.57	11.1	0.3	11.6	1.0	10.9	0.34
Y	6.34	0.12	6.10	0.12	6.00	0.35	5.44	0.02	5.41	0.21	5.72	0.12
Zr	4.89	0.36	4.45	0.24	5.24	0.72	4.54	0.48	5.35	1.28	4.90	0.49
Nb	1.72	0.12	1.73	0.04	1.89	0.09	1.48	0.06	1.39	0.07	1.53	0.01
Mo	4.43	0.23	3.09	0.23	2.81	0.16	2.50	0.10	2.59	0.17	2.74	0.18
Cs	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*	
Ba	20.0	2.2	17.0	0.3	16.7	0.95	16.9	0.5	20.5	2.3	17.6	0.50
La	3.32	0.13	3.27	0.11	3.19	0.17	2.76	0.08	3.18	0.42	2.87	0.07
Ce	5.34	0.16	5.21	0.13	5.07	0.32	4.99	0.10	5.16	0.35	5.07	0.11
Pr	0.76	0.02	0.72	0.03	0.70	0.04	0.64	0.02	0.80	0.18	0.65	0.01
Nd	3.21	0.07	2.88	0.11	2.85	0.24	2.59	0.02	2.82	0.31	2.57	0.11
Sm	0.69	0.06	0.58	0.02	0.58	0.06	0.54	0.01	0.66	0.13	0.52	0.02
Eu	0.25	0.02	0.23	0.01	0.23	0.02	0.20	0.01	0.20	0.005	0.20	0.01
Gd	0.76	0.02	0.77	0.02	0.76	0.06	0.72	0.02	0.70	0.02	0.68	0.03
Tb	0.14	0.02	0.11	0.002	0.11	0.01	<L.D.*		<L.D.*		<L.D.*	
Dy	0.87	0.04	0.83	0.02	0.85	0.04	0.79	0.02	0.75	0.01	0.76	0.01
Ho	0.20	0.01	0.18	0.004	0.18	0.01	0.17	0.01	0.17	0.003	0.16	0.004
Er	0.64	0.03	0.60	0.004	0.61	0.02	0.54	0.01	0.61	0.07	0.52	0.02
Tm	0.12	0.01	0.12	0.003	0.10	0.03	0.11	0.004	0.24		<L.D.*	
Yb	0.63	0.04	0.56	0.01	0.54	0.05	0.52	0.02	0.51	0.03	0.49	0.02
Lu	0.08	0.01	0.07	0.004	0.07	0.01	0.07	0.005	0.07	0.003	0.07	0.004
Hf	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*	
Ta	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*	
Tl	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*	
Pb	<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*		<L.D.*	
Bi	0.13	0.02	<0.09		<0.09		<L.D.*		<L.D.*		<L.D.*	
Th	0.11	0.02	0.11	0.01	0.11	0.02	0.77	0.66	0.08		0.08	0.01
U	<L.D.*		<L.D.*		<L.D.*		<L.D.*		0.14		<L.D.*	

*Concentrations below L.D. of the instrument. Note that it was not possible to determine several elemental concentrations (<L.D.), for those elements, the s($\bar{x}$) was not determined either. All the elemental concentrations are in ppm.

Table 16. CV-0-A, CV-0-B, CV-1, CV-5 & CV-10 (2 months later).

	CV-0-A			CV-0-B			CV-1			CV-5			CV-10		
Element	**T0**	**T9**	**T10**	**T0**	**T9**	**T10**	**T0**	**T9**	**T10**	**T0**	**T9**	**T10**	**T0**	**T9**	**T10**
Li	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Ti	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	179	173	183	194	220	216	144	154	165
V	<8*	<8*	<8*	8.6	10.0	11.8	17.5	16.0	17.4	16.3	18.2	19.9	14.9	15.3	17.0
Cr	335	415	375	801	646	609	620	577	608	512	568	734	604	602	699
Rb	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Sr	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Y	2.8	3.1	3.2	2.9	3.4	4.0	6.1	5.9	6.3	6.6	7.1	6.6	6.3	6.7	6.2
Zr	<L.D.*	<L.D.*	<L.D.*	2.9	4.4	5.9	6.5	6.0	6.8	5.9	6.8	5.4	5.2	5.8	5.3
Nb	<L.D.*	<L.D.*	<L.D.*	0.7	1.4	2.0	2.4	2.6	2.9	2.5	2.8	2.2	<2*	<2*	<2*
Mo	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Cs	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Ba	21.9	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	16.9	18.1	19.0	20.5	22.4	<L.D.*	<L.D.*	<L.D.*	<L.D.*
La	1.3	1.2	<0.9*	1.5	1.8	1.9	3.7	3.6	4.0	3.6	3.9	3.4	3.2	3.4	3.2
Ce	3.2	3.1	3.1	2.8	3.2	3.2	6.2	6.0	6.6	5.4	5.7	5.2	5.4	5.6	5.3
Pr	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	0.8	0.8	1.0	0.9	1.1	0.9	0.8	0.8	0.8
Nd	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	6.92	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Sm	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Eu	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Gd	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Tb	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Dy	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	1.75	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Ho	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	0.37	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Er	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	1.45	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Tm	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Yb	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Lu	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Hf	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Ta	2.21	2.27	2.24	2.24	2.25	2.25	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Tl	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Pb	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Bi	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Th	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
U	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*

* Concentrations below the L.D. of the instrument. Note that all the trials and all the samples were analyzed in triplicates.

Chapter 4

Determination of Environmental Mobility of HFSE and REE in Samples

It is not uncommon for the original composition of geologic materials to be changed by some alteration process involving fluids that break down constituent minerals and mobilize various elements. Depending on the nature and intensity of the alteration process, however, only some elements are affected (i.e. mobile) whereas others are largely unaffected (i.e. immobile). Environmental mobility is a geochemical characteristic of an element and can occur when an element has been subjected to high temperature hydrothermal alteration or to low temperature surficial weathering.

Elements such as HFSE, REE, Al, and Ti are known to be largely immobile (MacLean and Kranidiotis, 1987). In other words, the initial mass concentration or ratio of these immobile elements to one another does not change when the sample is subjected to high temperature and/or high pressure, or surficial weathering. This characteristic of HFES makes them useful as geochemical tracers in Earth Science. In fact, HFSE determination can be used to recognize primary composition of variably altered geologic materials and to monitor the mass gain or loss of mobile elements during alteration processes (MacLean and Kranidiotis, 1987). For this reason, the HFSE are part of this study that aimed to confirm the environmental immobility of HFSE and REE contained in fine-grained tailings exposed to weathering in Labrador. By comparison, the concentration of mobile elements such as alkali or transition metals is more likely to be reduced via losses during weathering of mine tailings. Any such losses of mobile

elements during weathering would be expected to increase as the age of the tailing increases. The determination of mobility of HFSE and REE is described in section 4.2 and 4.3.

4.1 Physical Characterization of the Samples

Prior to the determination of the environmental mobility of HFSE and REE in the IOC samples, a physical characterization of CV-0-A sample was done to gather ancillary data in support of the geochemical (mobility) determination. In addition, IOC requested information concerning the presence or absence of amphiboles in their tailings (that are often associated with Ti and may interfere with the concentration operations in IOC). For that reason, the physical characterization of the samples included a mineral separation using heavy liquids, followed by a grain size determination and investigation using an electron probe microanalyser (EPMA). The heavy liquid separation aided in the determination of the mineralogy of the samples, while the grain size measurement aided in the determination of the mean grain size of the mineral particles.

The sample CV-0-A was selected to undergo the physical characterization due to the large quantity available compared with the other samples. Moreover, CV-0-A was never exposed to weathering; therefore, it presented an ideal starting composition of the mine tailings. It is important to note that this research was limited to the investigation of elemental mobility of HFSE and REE. Therefore, determining the weathering effects on the mineral composition of the tailings were beyond the scope of this thesis research.

4.1.1 Mineral Separation using Heavy Liquids

The separation of minerals using heavy liquids is a physical process used to fractionate materials of different densities based upon their buoyancy. This separation was done to concentrate higher density minerals, in which HFSE were suspected to be present. In this procedure, a sample is mixed with a heavy liquid, i.e. a high density fluid that has a known density. When the solid sample and the heavy liquid are mixed, the minerals with densities greater than the heavy liquid sink, the minerals with lower densities float, and the minerals with the same density remain suspended in the heavy liquid. For example, low density minerals such as clay and quartz float, while heavy minerals such as zircon sink (Jones, 1987, p. 31, Mebus and Schleicher, 1990).

In this part of the study, two heavy liquids, tribromomethane (IUPAC name), $CHBr_3$, and Iodomethane (IUPAC name), CH_3I, were used. These heavy liquids are commonly known as bromoform and methylene iodide, respectively. Bromoform has a density of 2.85 g/cm^3, a viscosity of 1.8 cP and a vapour pressure of 787 Pa. Methylene iodide has a density of 3.32 g/cm^3, a vapour pressure of 160 Pa, and a viscosity of 2.6 cP. The disadvantage of using these heavy liquids is their toxicity. Therefore, the process must be done in a fume hood. Since bromoform and methylene iodide were used, minerals were separated in three groups with densities of <2.85, >2.85 and <3.3, and >3.3 g/cm^3. Some grains of these three groups were mounted for subsequent elemental analysis using an EPMA.

The first step of the heavy liquid separation was to split the tailing sample (CV-0-A) in order to obtain a smaller representative sample. This sample was weighed and

labelled as **Non-pulverized Tailing Sample** (see Table 17). A photograph of a small but representative amount of the non-pulverized sample was taken using a binocular microscope with a magnification of 25X. Some grains of the photographed sample were placed on a flat, polished, epoxy mount with double sided tape, for further analysis using an EPMA.

In the second step of the separation, the unprocessed tailing sample was mixed with bromoform, vigorously stirred, and allowed to settle for thirty minutes. The light minerals were rinsed in acetone, collected, air dried, and weighed. This sample was labelled as **Minerals <2.85 g/cm^3**, indicating that minerals were lighter than bromoform. A smaller representative amount of this sample was taken and photographed through the binocular microscope (25X magnification). Some of the mineral grains with density <2.85 g/cm^3 were mounted next to the unprocessed tailing sample grains on the previously described epoxy mount.

The sunken heavy minerals from the previous step were used in the third step of the separation. These minerals were mixed with methylene iodide, vigorously stirred, and allowed to separate for thirty minutes. Again, the light and heavy minerals were rinsed with acetone and the samples were air dried. The samples were labelled **Minerals <3.3 g/cm^3** and **Minerals >3.3 g/cm^3**, respectively. Note that sample mineral <3.3 g/cm^3 had a density that ranged from 2.85 to 3.3 g/cm^3. A smaller representative amount of these samples was taken and photographed through the microscope and mounted (next to the sample grains of the unprocessed tailing sample and minerals <2.85 g/cm^3). The mount was then carbon coated for subsequent analyses using an EPMA.

Figures 14 to 17 are photographs, taken through a binocular microscope (25X magnification), that show minerals identified. Table 17 includes a description of the samples, masses, percentage of the total sample, and the identified minerals in these figures. The majority of the sample analyzed (CV-0-A) consisted of quartz, with some inclusions of magnetite. For that reason, some quartz grains sank in the bromoform or methylene iodide. The presence of larger grains of magnetite, with quartz inclusions, was also observed. The more dense portion of the tailing sample primarily consisted of Fe-containing minerals such as biotite, magnetite, garnet, limonite, and goethite. It is important to note that the mineral identification was done to support the geochemical (mobility) determination. Therefore, studies such as determination of percentage abundance of each phase in each of the different density fractions were beyond the scope of this thesis research.

Table 17. Heavy liquid separation of CV-0-A.

Label	Mass (g)	%	Identified minerals in photographs*
Non-pulverized Tailing Sample	14.74	100%	Predominantly qtz, some with mag inclusions. Minor amounts of Fe oxide/cb (Gt or Lm)
Minerals < 2.85 g/cm^3	9.98	68%	Major amount of qtz, some with mag inclusions. Presence of Fe oxide/cb (Gt or Lm)
Minerals < 3.3 g/cm3	2.02	14%	Qtz with mag inclusions Mag with qtz inclusions. Minor presence of Bt.
Minerals > 3.3 g/cm3	2.56	17%	Mag, Lm, Grt Some grains of qtz with mag inclusions.

* See list of abbreviations.

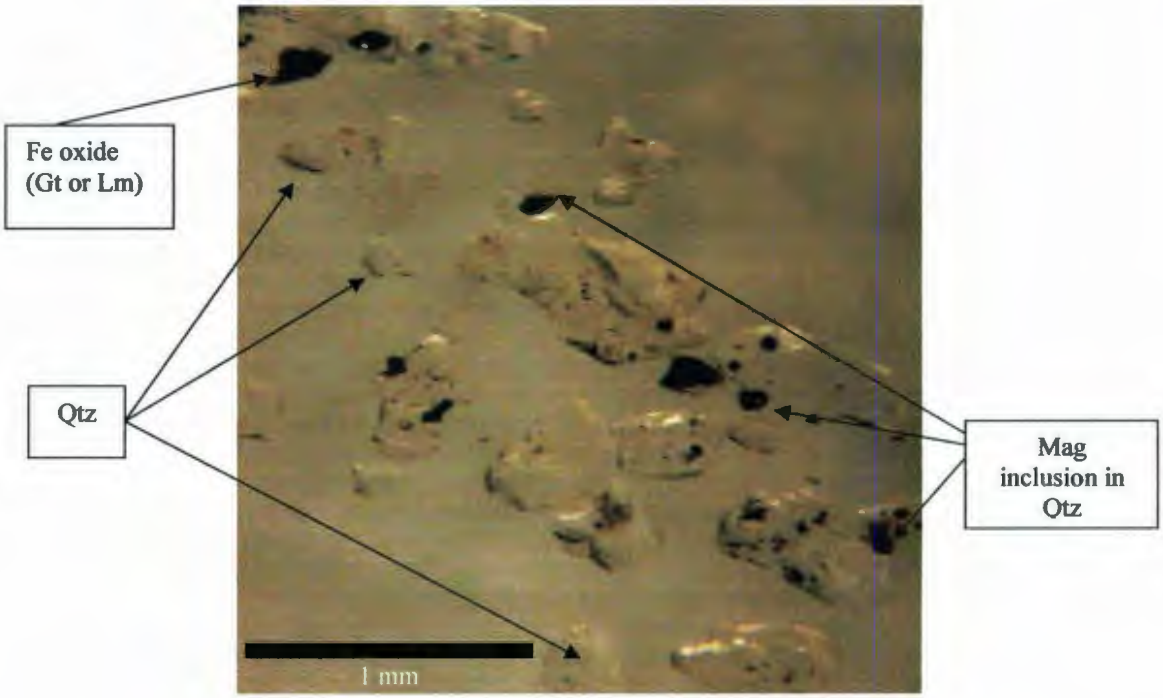


Figure 14. Non-pulverized tailing sample.

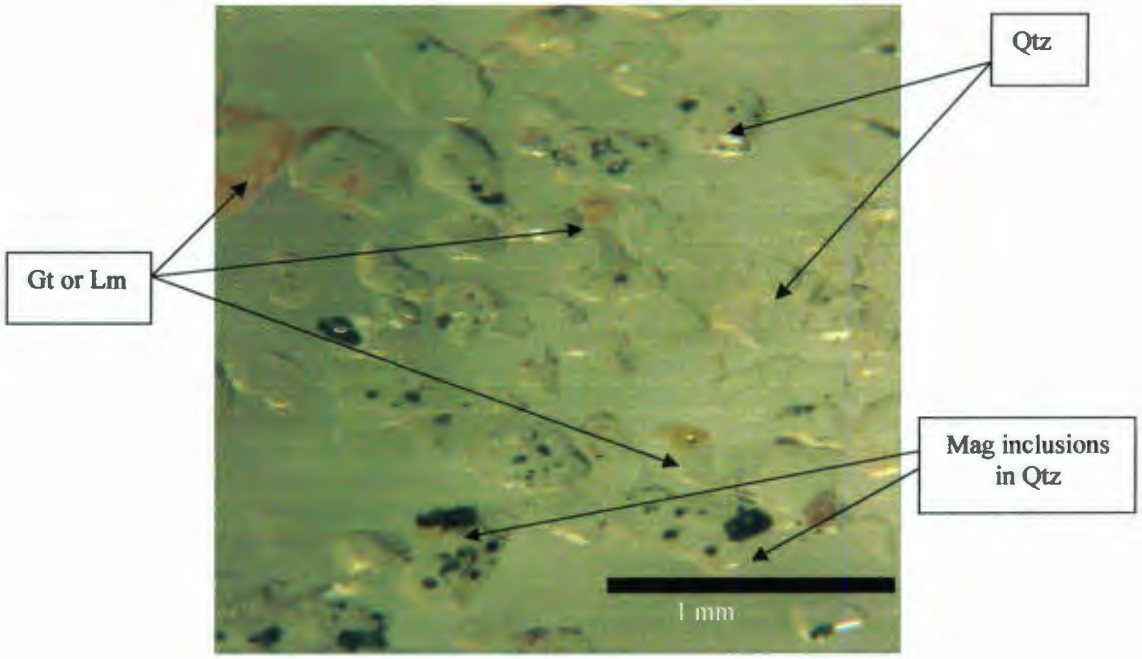


Figure 15. Minerals <2.85 g/cm^3.

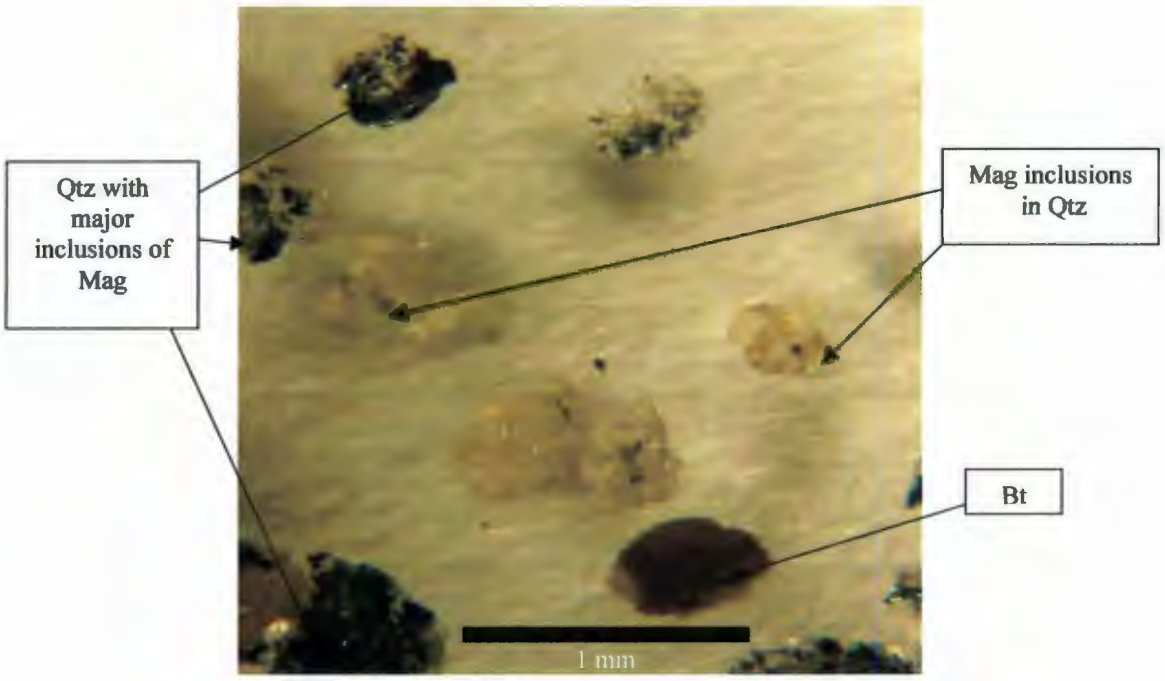


Figure 16. Minerals < 3.3 g/cm^3.

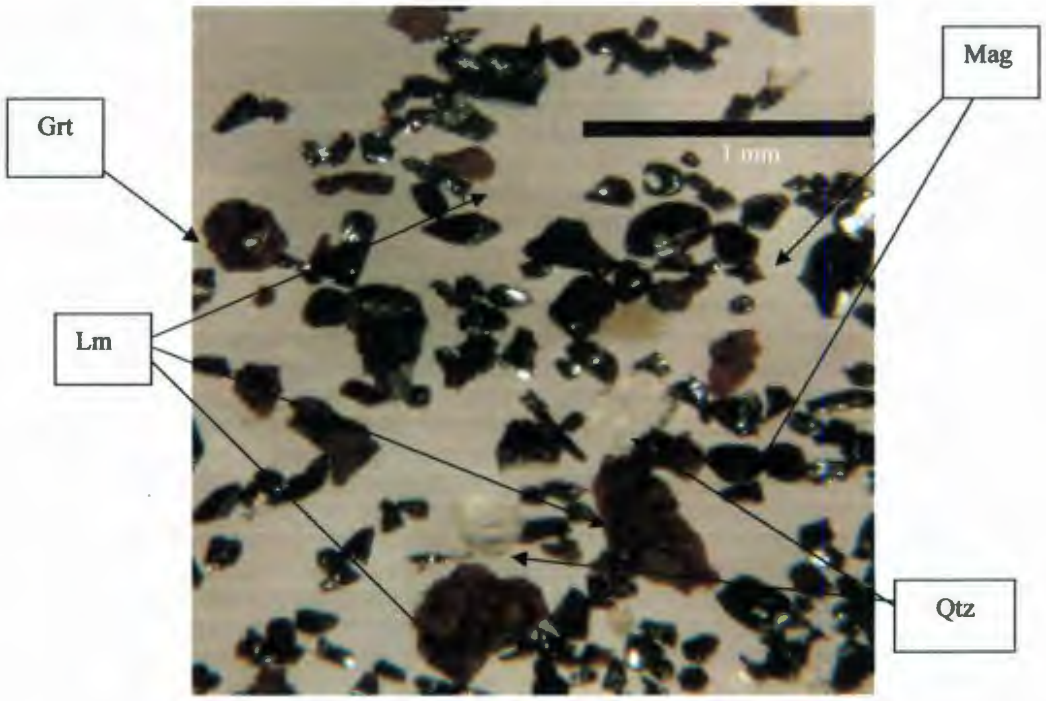
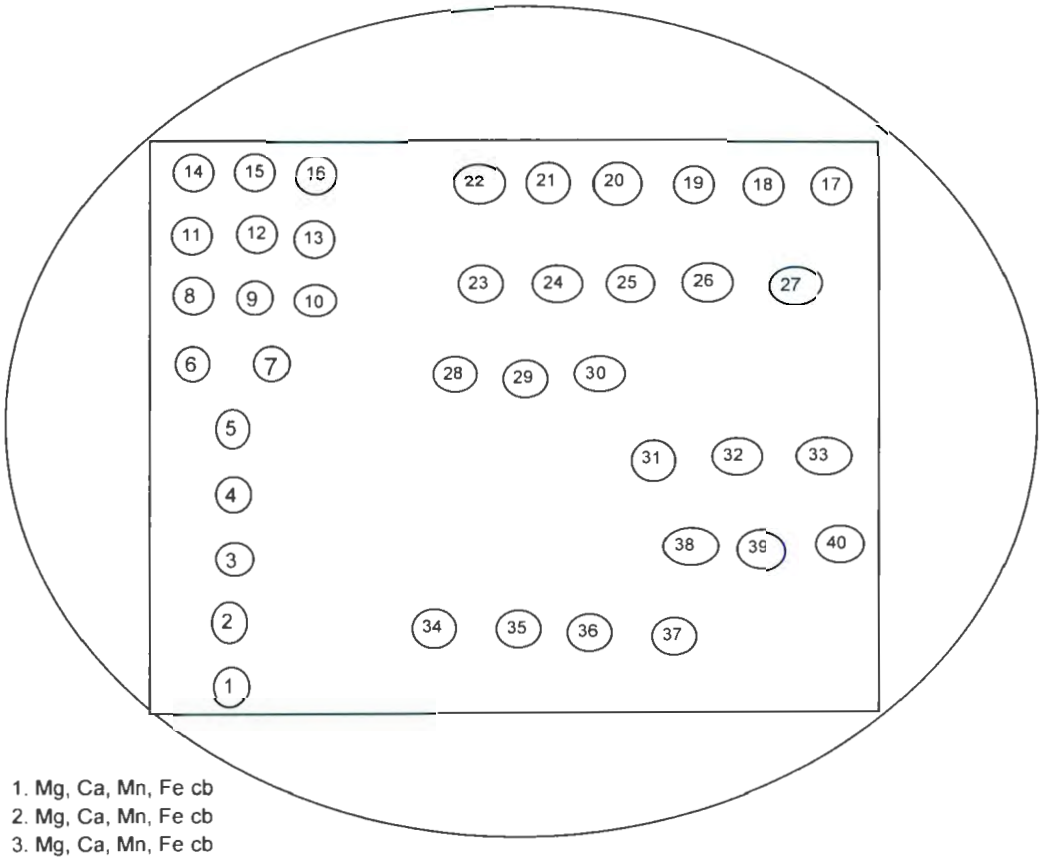


Figure 17. Minerals >3.3 g/cm^3.

The mineral grains mounted in epoxy were analyzed using an EPMA. This analysis produced qualitative elemental results; therefore, it was possible to determine the elements present in the sample but not their precise concentrations. In addition, this instrument cannot determine carbon or oxygen. From the results, the presence of Si, Mg, Ca, Mn, and Fe carbonates, could be deduced but not fully verified. In addition, the energy-dispersive X-Ray spectra (EDS) results suggested the presence of Fe and Al oxides. Some silicates including amphibole (grunerite), and almandine (garnet) were also found. It was not considered relevant to use photographs from the epoxy mount since an identification key of the epoxy mount was sketched. This identification key aided in the analysis using an electron microprobe. This identification key is shown in Figure 18. Appendix 26 contains the complete set of the EDS.

The EDS results generally agree with the optical mineral identification in the photographs. One difference was the presence of biotite in the minerals <3.33 g/cm^3. Biotite was not found in any of the EDS results. It is possible that biotite grains were not placed on the mount since only a small number of representative grains were mounted. In addition, the EDS suggested the presence of an amphibole mineral (grunerite). However, this mineral was not seen under the microscope in any of the mineral groups. As requested, the presence of amphibole was reported to IOC. Note that neither the EDS nor the observations under the microscope suggest the presence of zircon. Also, the amount of biotite and grunerite were minor components of the tailings.



1. Mg, Ca, Mn, Fe cb
2. Mg, Ca, Mn, Fe cb
3. Mg, Ca, Mn, Fe cb
4. Mg, Ca, Mn, Fe cb
5. Mg, Ca, Mn, Fe cb
6. Mg, Ca, Mn, Fe cb
7. Fe oxide
8. Mg, Ca, Mn, Fe cb
9. Mg, Ca, Mn, Fe cb
10. Fe oxide
11. Mg, Ca, Mn, Fe cb
12. Alm (grt)
13. Mg, Ca, Mn, Fe cb
14. Mg, Ca, Mn, Fe cb
15. Mg, Ca, Mn, Fe cb
16. Mg, Ca, Mn, Fe cb
17. Al oxide
18. Fe oxide
19. Al oxide
20. Fe oxide
21. Qtz with Fe oxide inclusion
22. Fe oxide
23. Qtz
24. Am (gru)
25. Amphibole or garnet
26. Qtz with Fe oxide inclusion
27. Fe oxide
28. Fe oxide
29. Fe oxide
30. Fe oxide
31. Fe oxide
32. Fe oxide
33. Fe oxide
34. Quartz
35. Mg, Ca, Mn, Fe cb
36. Mg, Ca, Mn, Fe cb
37. Quartz
38. Fe oxide
39. Am (gru)
40. Am (gru)

Figure 18. Identification key of the SEM epoxy mount (see list of abbreviations).

4.1.2 Grain Size Measurement

Two measurements of grain size were done on one sample, CV-0-A. The first measurement was done on the original tailing sample as provided by IOC (non-pulverized CV-0-A). The second measurement was done on the same material that has been further pulverized at MUN (pulverized CV-0-A). The examination of the former sample was to assess grain size variation in the original starting tailing material. The second measurement was done to asses the grain size effect related to the crushing procedure employed at MUN. The test was done using sample CV-0-A because this sample was available in larger amounts compared to the other samples. In addition, CV-0-A is a typical sample, least weathered and ultimately this study focussed on the geochemical characteristics of this sample. Therefore, the grain size distribution was of lesser interest.

For the grain size measurements, fourteen sieves were used and they were shaken manually. Grain size measurement results of the non-pulverized sample are shown in Table 18 and Figure 19. Grain size measurement results of the pulverized sample are shown in Table 19 and Figure 20. These results show that the majority of the non-pulverized sample had grain sizes which ranged from 90 μm to 300 μm. In addition, the results show that the majority of the pulverized sample had grain sizes ranging from 45 μm to 180 μm.

Table 18. Size grain measurement of non-pulverized sample (CV-0-A).

Sample: CV - 0 - A (not pulverized)				
Sieve #	**Size**	**Weight (g)**	**Weight Passing (g)**	**% Passing**
10	2 mm	0.08449	0.08449	0.19
18	1 mm	2.15182	2.23631	5.05
20	850 µm	0.33182	2.56813	5.80
30	600 µm	2.27616	4.84429	10.94
40	425 µm	2.33870	7.18299	16.21
50	300 µm	5.26083	12.44382	28.09
60	250 µm	4.08220	16.52602	37.30
80	180 µm	7.94134	24.46736	55.23
100	150 µm	3.96437	28.43173	64.18
120	125 µm	3.58401	32.01574	72.27
170	90 µm	5.39718	37.41292	84.45
200	75 µm	2.05037	39.46329	89.08
230	63 µm	1.33910	40.80239	92.10
325	45 µm	1.84755	42.64994	96.27
< 325	<45 µm	1.65026	44.30020	100
	Total	44.30020		

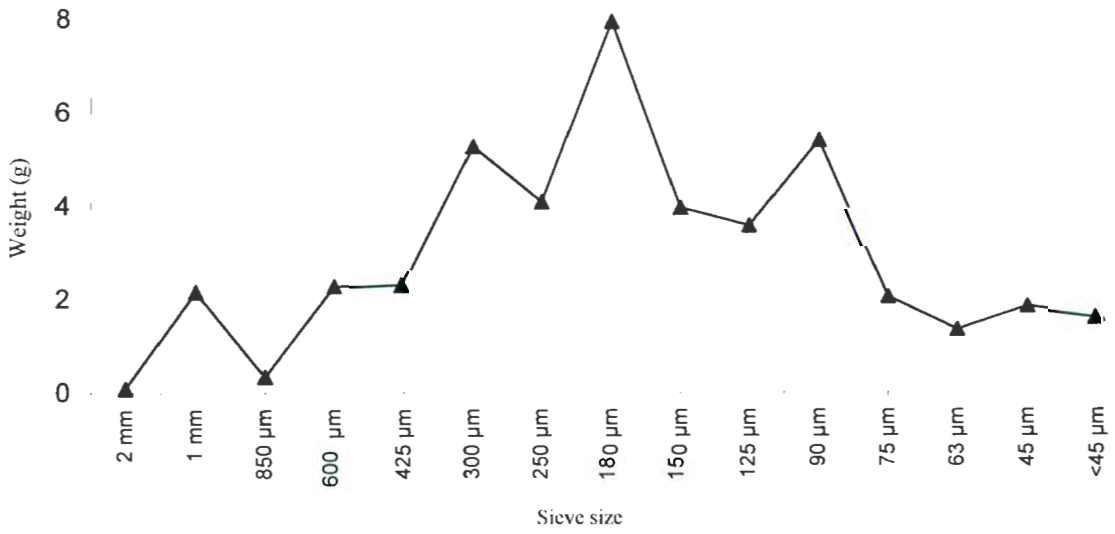


Figure 19. Grain size distribution of non-pulverized sample (CV-0-A).

Table 19. Size grain measurement of pulverized sample (CV-0-A).

Sample: CV - 0 - A (pulverized)				
Sieve #	**Size**	**Weight (g)**	**Weight Passing (g)**	**% Passing**
10	2 mm	0.01700	0.01700	0.028
18	1 mm	0.09258	0.10958	0.179
20	850 µm	0.02176	0.13134	0.215
30	600 µm	0.18030	0.31164	0.510
40	425 µm	0.23000	0.54164	0.887
50	300 µm	0.64706	1.18870	1.946
60	250 µm	0.89250	2.08120	3.408
80	180 µm	3.46557	5.54677	9.083
100	150 µm	4.61652	10.16329	16.642
120	125 µm	7.35860	17.52189	28.692
170	90 µm	16.76913	34.29102	56.151
200	75 µm	7.73775	42.02877	68.821
230	63 µm	9.70678	51.73555	84.716
325	45 µm	7.08288	58.81843	96.314
< 325	<45 µm	2.25096	61.06939	100
	Total	61.06939		

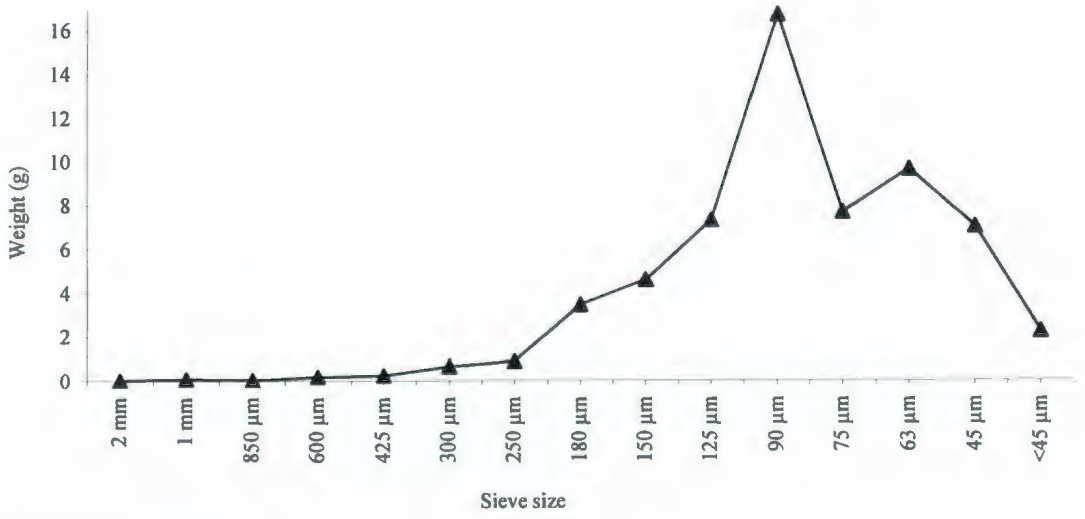


Figure 20. Grain size distribution of pulverized sample (CV-0-A).

4.2 Determination of Environmental Mobility of HFSE and REE on Tailing Samples from IOC

The determination of environmental mobility of HFSE and REE was done once the physical characterization of the sample was completed. In order to assess environmental mobility or immobility of HFSE and REE, the compositions of different aged tailing samples (weathered for 0-10 years) were compared. Tables 4 and 15 show the results of multiple analyses of these samples. Samples were analyzed using the acid digestion procedure, previously described in section 1.2.1. This procedure was used because the method development of optimization confirmed that the original parameters of the acid digestion were optimal (see results in Table 4). The variations in concentration of Ti, V, Cr, Rb, Sr, Y, Zr, Nb and Th were plotted according to the age of the tailing samples. As previously mentioned in Table 1, CV-0-A was a tailing sample that was never subjected to weathering. Therefore, its age is given as zero years and is plotted as the first point (t=0) on the axis in Figures 21 to 29. The remaining tailing samples are organized according to increasing age: CV-0-B (t=<1), CV-1 (t=1), CV-5 (t=5) and CV-10 (t=10). Note that the error bars in these figures represent one standard deviation of the mean (corresponding to Table 4).

Assessing changes in the composition of different aged tailing samples is a complicated endeavour because IOC mined different ores over the years and it is not known how many types of ores were used. Therefore, comparing one age of tailing sample to another is potentially complicated depending on how many different the ores were over the years. However, normalized ratios of analyses of tailing samples can be

used to assess whether there were significant geochemical differences in the elements of interest to this study (i.e. HFSE, REE). Lastly, the very low concentrations of the majority of the elements of interest present (i.e. concentrations close to the L.D. of the ICP-MS) also increase the difficulty of this comparison of different aged tailing samples.

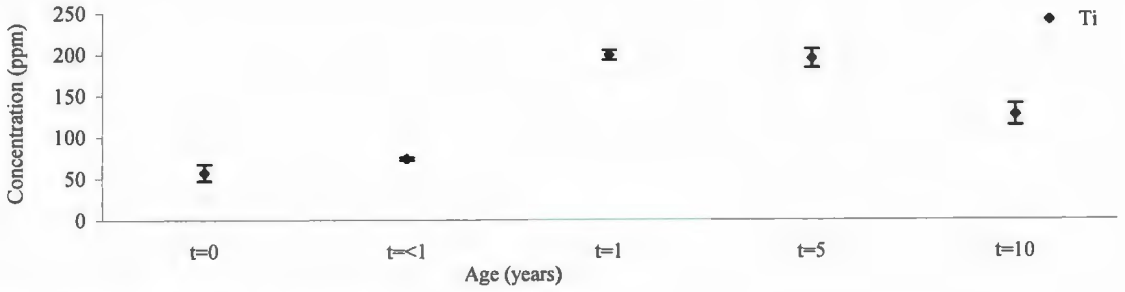


Figure 21. Variation of Ti with age.

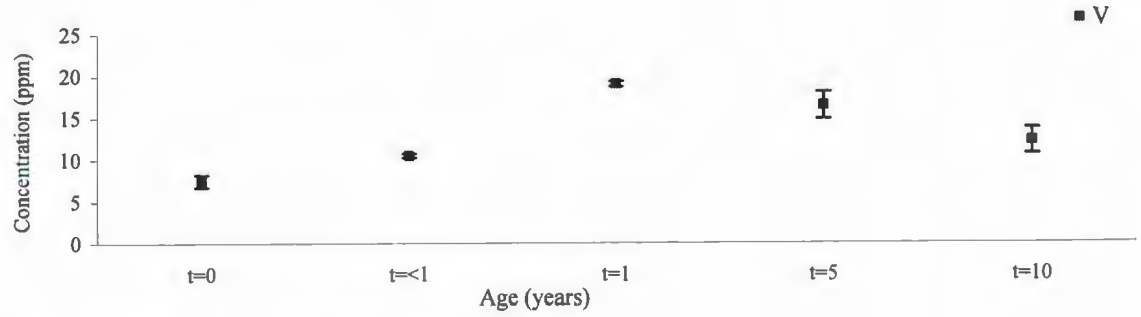


Figure 22. Variation of V with age.

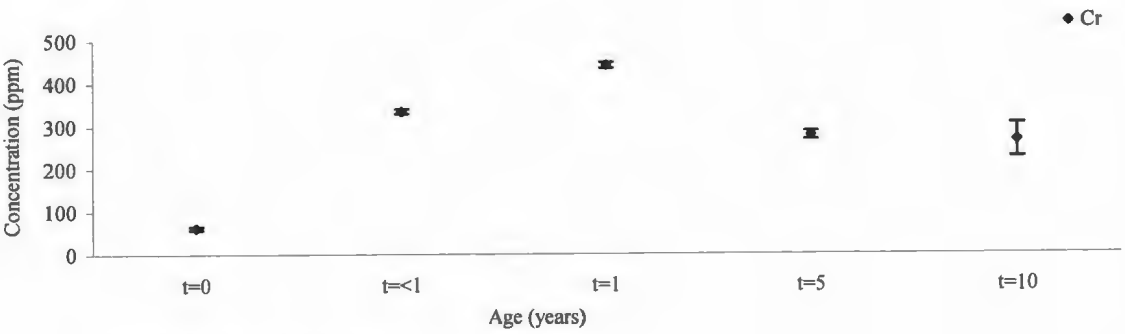


Figure 23. Variation of Cr with age.

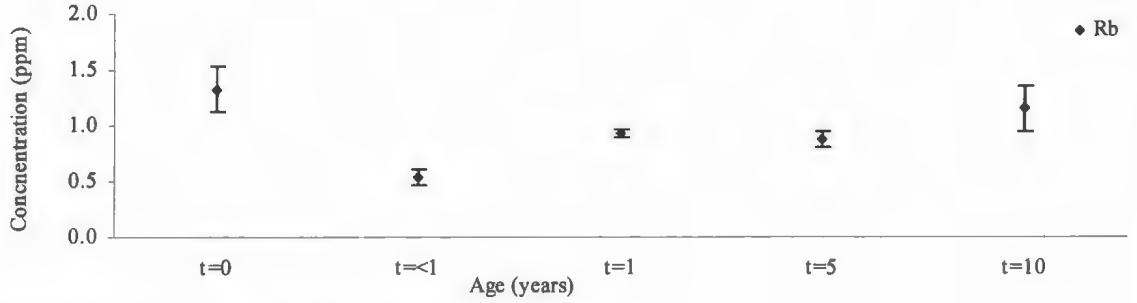


Figure 24. Variation of Rb with age.

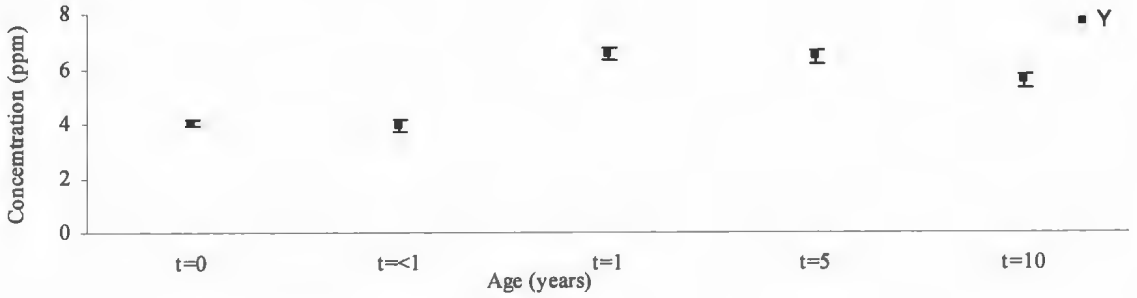


Figure 25. Variation of Y with age.

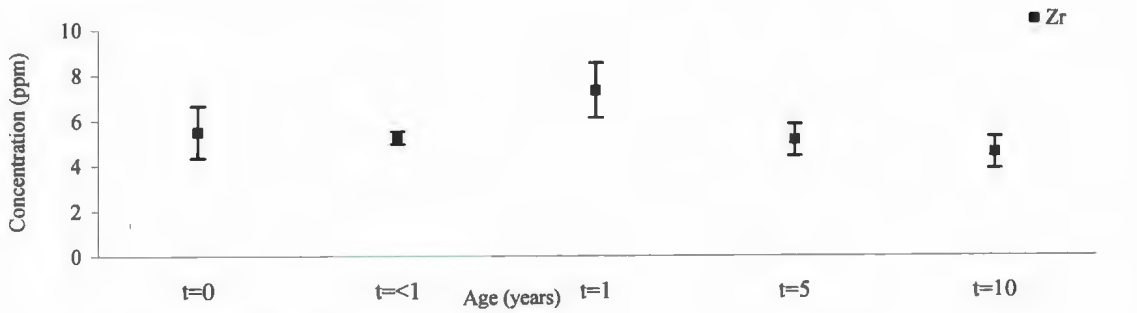


Figure 26. Variation of Zr with age.

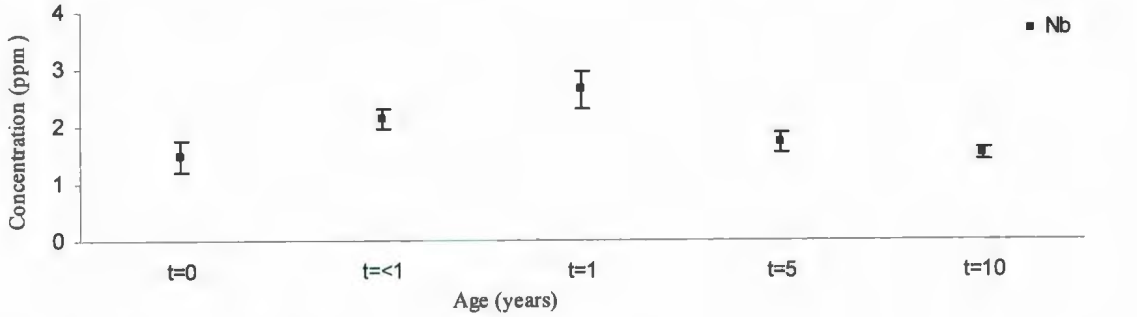


Figure 27. Variation of Nb with age.

Figure 28. Variation of Th with age.

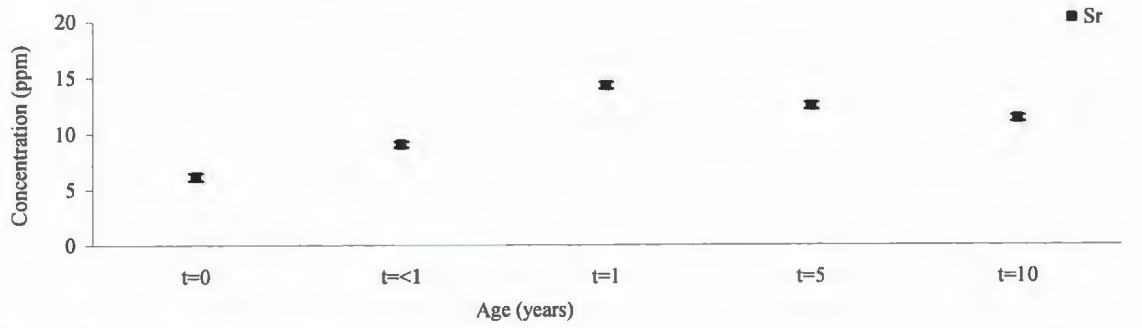


Figure 29. Variation of Sr with age.

In the study of the different aged tailing samples, it was expected to observe a decreasing trend of concentration of mobile elements and a near-constant concentration of HFSE, which are considered immobile. However, this was not the case. Mobile and immobile elements both showed variations in their concentrations with respect to time. In fact, HFSE abundances in different tailing samples showed some statistical variations when a t-Test was performed, in particular, on results for Zr, Nb, and Th (See Table 20). For example, t-test values between CV-0-A and CV-1 for Zr, Nb, and Th were 3.32, 6.7, and 9.52 respectively. In addition, CV-0-A and CV-0-B showed t-Test values for Nb of 4.97 (t-Test critical value was 2.78 for a confidence level of 95% and 4 degrees of freedom). The other HFSE were not included in the statistical t-Test since their

concentrations were near or below the L.D. of the ICP-MS. The mentioned high t-Test values suggested that the different aged tailing samples may belong to different precursors or ore types. CV-0-A and CV-0-B showed t-Test values for Nb of 4.97.

Table 20: t-Test for environmental mobility

	CV-0-A / CV-0-B	CV-0-A / CV-1	CV-0-A / CV-5	CV-0-A / 10
Zr	-0.63	3.32	-0.69	-1.78
Nb	4.97	6.7	1.97	0.22
Th	0.35	9.52	1.53	1.04

Another possible reason for these variations in HFSE among different aged tailing samples may be mass gain or loss (i.e. HFSE mobility), or alternatively, changes in the abundance of minerals that contain no HFSE (e.g. quartz) that would lead to dilution of these elements in the tailings. In order to resolve this issue, the results of the chemical analyses of the different aged tailing samples were plotted on multi-element diagrams normalized to a PM-composition and also normalized to the zero-age tailing sample CV-0-A. These normalized diagrams are shown and discussed in sections 4.3.1 and 4.3.2. Explanations about normalization to PM can be review in section 3.2.4.

4.3 Multi-element Normalization Diagrams of Tailing Samples

As previously explained in section 3.2.4, samples were normalized to ease the comparison of the tailings. In this part of the study, the tailing samples were not only normalized to the composition of the PM but also to the composition of sample CV-0-A.

The PM-normalized ratios of the elemental concentrations of the tailing samples are plotted on a logarithmic scale in Figures 30 and 31. The different aged tailing samples, normalized to sample CV-0-A (t=0), are shown in Figures 32 and 33. These figures portray the tailing samples by their age rather than their sample numbers (see Table 1).

4.3.1 Normalization of the Tailing Samples to PM

Figure 30 shows the elemental concentrations of REE in tailing samples normalized to PM values, while Figure 31 shows normalized values of REE and HFSE also normalized to PM. Note that REE were plotted alone in Figure 30 to facilitate the interpretation of the data and to present the geological coherence in that family. These graphs also show 1 σ error bars for each PM normalized element ratio that represent the relative standard deviation of the mean of each element (See formulas and results in Appendix 3 and Table 4, respectively). In these figures, a parallel trend exists among the different aged tailing samples, with the exception of Cr. Tailing sample CV-0-A (or t=0) has a significantly lower concentration of Cr in comparison with the rest of the tailing samples and Cr is also somewhat variable in samples t=<1 and t=5 (Figure 31). The somewhat inconsistent behaviour of Cr in most of the tailing samples reflects, in part, the low concentrations of Cr (the lowest normalized values). With the exception of Cr, however, the rest of the HFSE and REE follow a parallel trend.

The general low slope of the PM normalized patterns and their regular, smooth shapes are typical of common igneous and sedimentary rocks (Rollinson, 1993). Moreover, these smooth PM normalized patterns suggest that none of the HFSE or REEs

have been selectively affected (i.e. mobilized) with respect to one another during the weathering process, regardless of the age of the tailing sample. In addition, the similarity (i.e. parallel nature) of the PM normalized patterns for the different aged tailing samples suggests that even if different ore types were mined over the ten years represented in this study, the HFSE and REE characteristics of these ore types are controlled by a common set of trace minerals in the ores that are remarkably similar to one another. From the perspective of the HFSE and REE, it appears as if there is one type or one trace element composition of ore. Although it is likely that different types of ore were mined in the ten year period that this study covers, the HFSE and REE data imply only one composition of ore, which makes assessing the relative environmental mobility of HFSE and REE much more straightforward. Little to no mobility is discernible except, perhaps, for V, Ti, and Cr. It is possible, however, that the source of these scattered results (V, Ti, Cr concentrations) might be the steel-based crushing/milling process. This process is expected to influence these transition metals but not the HFSE or REE. It is important to note that this research was focussed on the environmental mobility of HFSE and REE. Therefore, the potential alterations that samples may undergo during the extraction or concentration of the iron ore processing (crushing, milling, etc) are beyond the scope of the research. For that reason, these scattered results (concentrations of V, Ti, and Cr) were not further investigated.

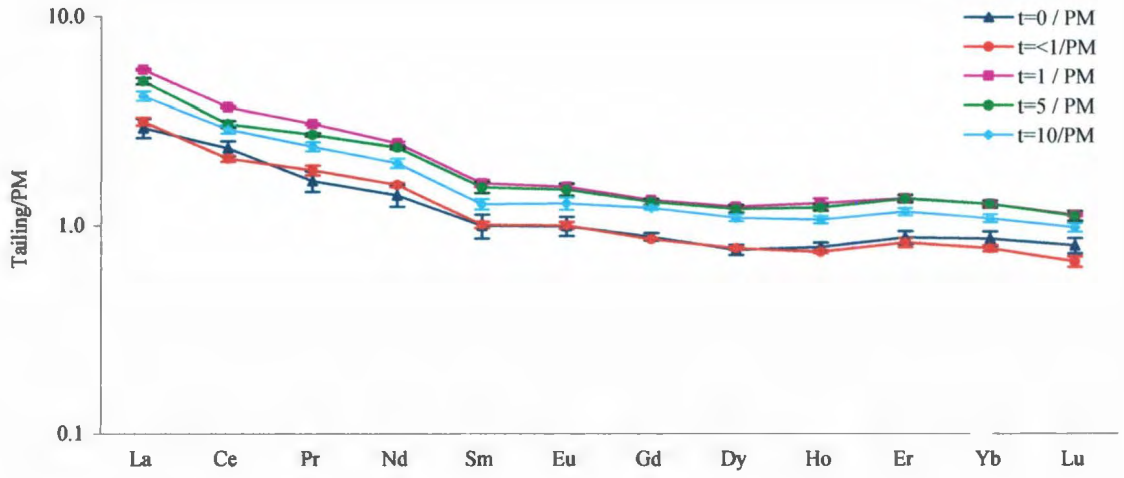


Figure 30. REEs in different aged tailing samples normalized to PM.

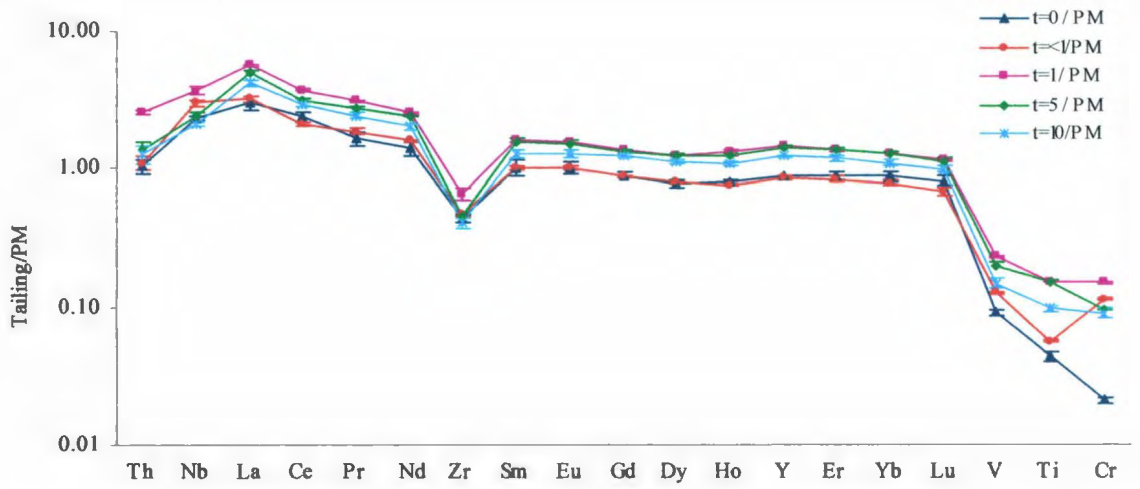


Figure 31. REEs and HFSE in different aged tailing samples normalized to PM.

4.3.2 Normalization of the Tailing Sample to t=0

The normalization of different aged tailing samples to sample t=0 was done to emphasize the small but systematic differences in absolute concentration of HFSE and REE that exist among the samples. Figure 32 shows the concentration of REE in different aged tailing samples normalized to REE in sample t=0, while Figure 33 shows

normalized HFSE and REE. As previously mentioned, REE were plotted separate to facilitate the interpretation of the data and to present the geological coherence in the REE family. It is important to note that each error bar represents 1 σ and was calculated using the relative standard deviation of the mean of the samples (See appendix 3 – r.s.d. A/B and results for r.s.d in Table 4). In these figures, similar to the PM diagrams described above, a generally parallel trend exists among the different aged tailing samples. Also, Cr does not follow this parallel trend (Figure 33). These diagrams further support the conclusion that time has not affected the mobility of HFSE or REEs in the tailing samples.

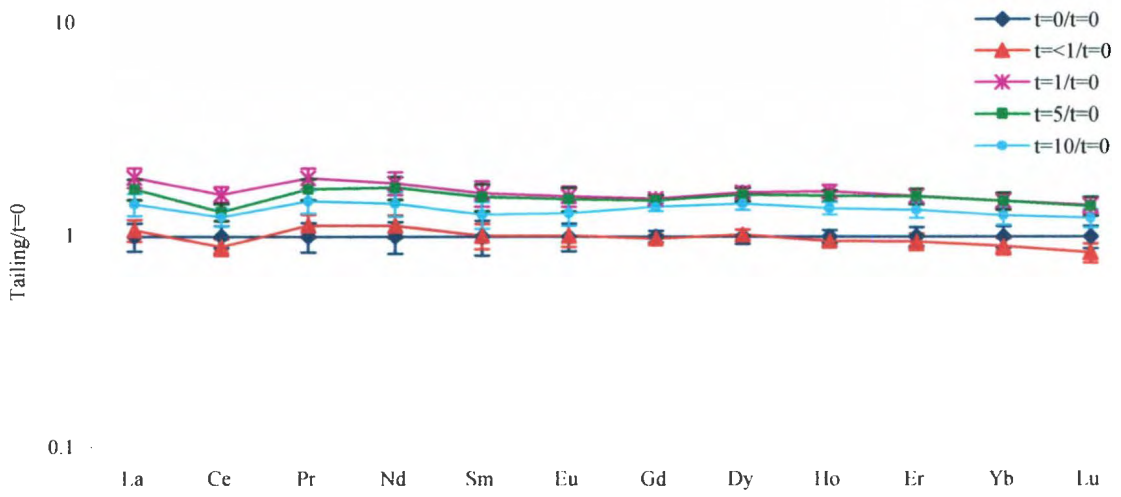


Figure 32. REEs in different aged tailing samples normalized to sample t=0.

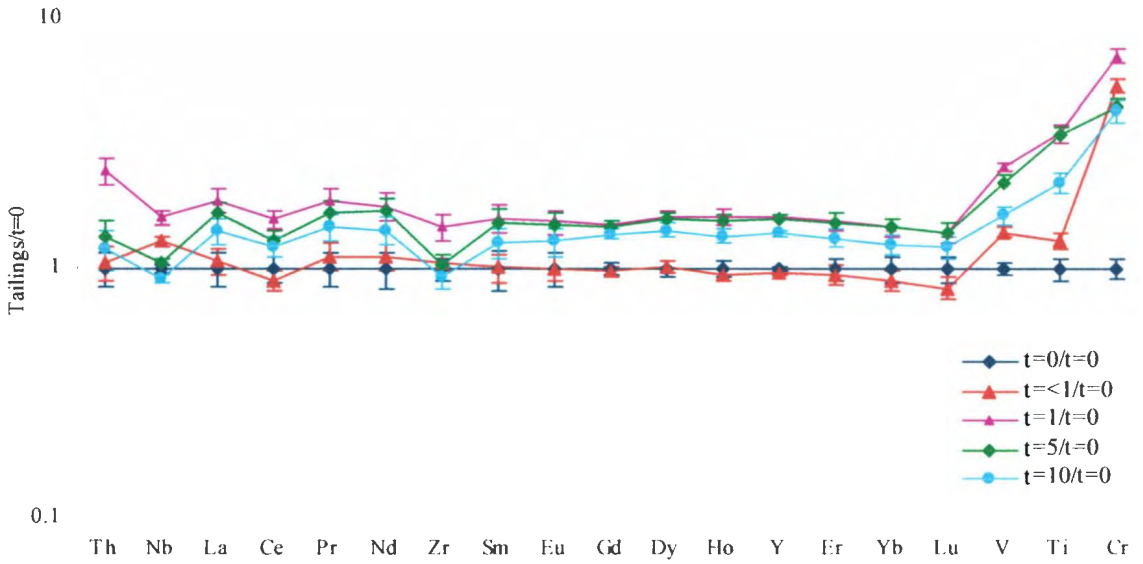


Figure 33. REEs and HFSE in different aged tailing samples normalized to t=0.

Samples t=0 and t<1 have virtually identical concentrations overlapping of HFSE and REE (except for Cr) suggesting that these two samples have an identical precursor or parent. The parallel HFSE and REE normalized patterns of all of the samples suggest that they share a common precursor. However, the small and systematic offset of the normalized patterns above that of t=0 is interpreted to be due to a dilution factor introduced by a mineral such as quartz which contains no HFSE or REEs. Quartz is by far the most abundant mineral constituent of all of the tailing samples. Based on the offsets in the normalized patterns, a dilution factor of approximately two can account for the range of HFSE and REEs abundances. Therefore, HFSE and REEs are slightly less concentrated in younger tailings than in older tailing samples, due to the addition of quartz.

Chapter 5

Conclusions

In the last decade, the use of ICP-MS in environmental geochemical analysis has increased and several systematic improvements in this instrument have been developed. These improvements included increased sensitivity, and higher sample throughput. Improvements in sample preparation procedures, however, have been neglected. For that reason, this study focused on a method development for acid digestion using ICP-MS, which was subsequently applied to determine environmental mobility.

This research, a multi-disciplinary study that linked concepts from geology, chemistry, and environmental science, accomplished two substantial goals: 1) method development to optimize an acid digestion procedure for HFSE using ICP-MS; and 2) assessment of environmental mobility of HFSE and REE in variably aged IOC tailing samples. In this research, samples from IOC were used, first of all, because the company agreed to assist and support this study. Also, the samples were obtained from a mine that is currently operating in the province of Newfoundland and Labrador. Environmental mobility studies are generally carried out for non-operating mines. Furthermore, IOC supplied a sample that was not exposed to weathering, which gave an ideal starting composition or baseline for the study of mobility.

The method development to optimize the acid digestion procedure used at MUN was an important part of the study. It consisted of a series of experiments that tested three variables of the procedure: 1) length of digestion; 2) acid mixture used; and 3) stability of

the resulting solution (a stable solution is defined as a solution that would maintain analytes in solution over time). These experiments revealed that the original parameters used in this procedure, were optimal. It was concluded that the original procedure, which has been used for over a decade at MUN, was the most efficient. For that reason, the original acid digestion procedure was used in the investigation of environmental mobility of HFSE and REE in the fine-grained mine tailing samples.

The study of environmental mobility, described in Chapter 4, consisted of the assessment of changes in the composition of different aged tailing samples. For this, the variations in concentrations of Ti, V, Cr, Rb, Sr, Y, Zr, Nb and Th were plotted. These figures showed unexpected variations in the concentrations of mobile and immobile elements with respect to time. For this reason, the elemental chemical composition of the tailing samples was normalized to the PM concentrations and to tailing sample CV-0-A in order to better interpret the variations in concentration. The normalized data show a parallel trend with the exception of V, Ti, and Cr. This parallel trend showed a typical pattern of PM normalized igneous and sedimentary rocks. Thus, these smooth PM normalized patterns suggest that none of the HFSE or REE were mobilized relative to one another during weathering.

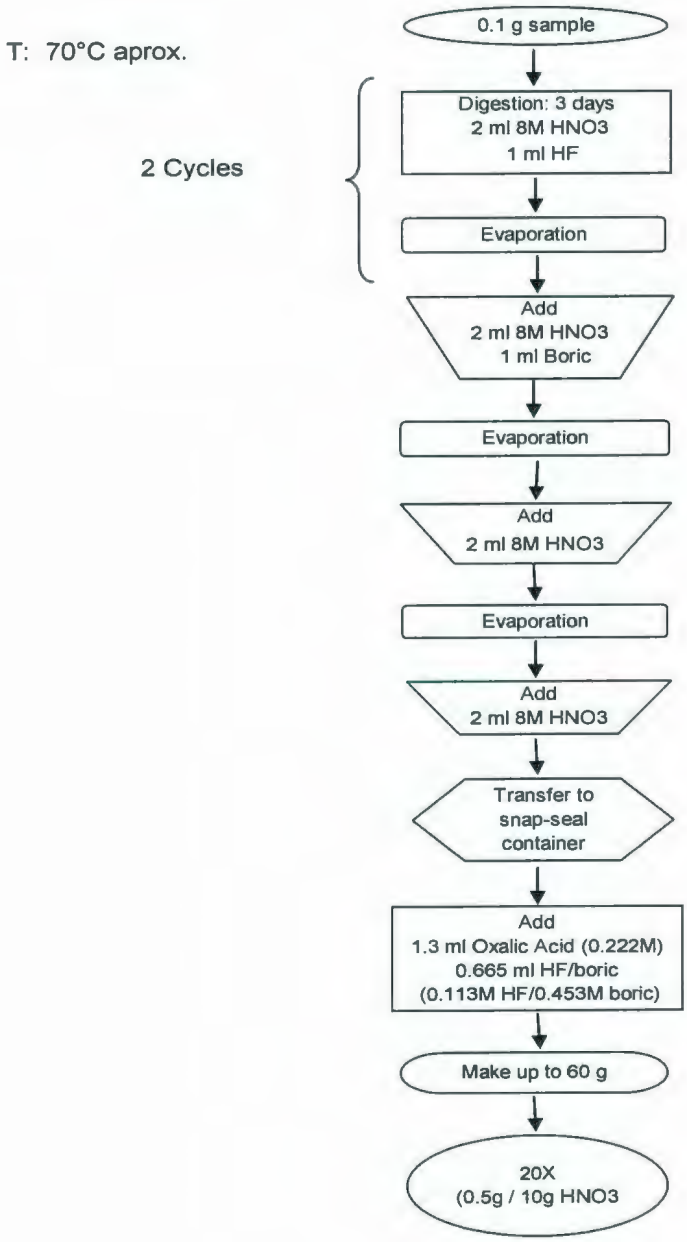
From the evaluation of HFSE and REE environmental mobility, it was concluded that no mobility was discernible. The small and systematic offset of the normalized patterns (Figures 30 to 33) is interpreted to be due to a dilution factor most likely introduced by quartz which contains no (or almost no) HFSE or REE. Based on the offsets in the normalized patterns, a dilution factor of approximately two can account for the range of HFSE and REE concentrations observed. That is, the elemental

concentrations of HFSE and REE in younger tailing samples are slightly less than the older tailing samples due simply to the addition of quartz. It is important to note that the normalized patterns showed scatter in the V, Ti, and Cr concentrations. These results, however, were interpreted to be caused by the steel-based crushing/milling process (during concentration and extraction of the ore).

Future research may include additional sampling that would lead to the determination of other sources of the scatter in the V, Ti, and Cr concentrations. In addition, future research to optimize the acid digestion procedure could include additional sampling of the mine tailing dumps and more replicates of the acid digestion procedure. This additional information could insure a better quantification of the analyte concentrations. Future research could also include more experiments that test stability of a solution in order to determine the length of time that a solution remains stable (re-analyzing samples after a week, two weeks, etc).

Appendixes

Appendix 1. T0 – Original acid digestion procedure.



Appendix 2. Extraction and concentration process of IOC.

The IOC mining operations consist of a series of processes that aim to separate iron bearing minerals from waste. These processes include physical extraction and concentration of these minerals. In the physical extraction process the ores are mined, while in the concentration process the content of iron is enriched. During the extraction, holes are drilled and filled with explosive products. Following the explosion, the ore is mined using loaders and electrical shovels. Then it is transported by trucks to feed an automatic train operation, which transports the ore to primary crushers. In these crushers, the size of the ore is reduced (IOC, 2008a).

The iron concentration process consists of a sequence of steps that upgrade ore from approximately 39% to 67%. The iron bearing minerals are separated from the waste material and recovered in three processing areas: The Primary Spiral Plant, the Magnetite Plant, and the Hematite Plant. The concentration process starts by milling the already crushed material in a grinding mill. The smaller particles produced are pumped to the Primary Spiral Plant which utilizes gravity separation methods to separate iron bearing minerals. These methods include a combination of hydro-cyclones, hindered-settlers, and spiral separators. The heavy material is recovered and sold as concentrate, while the unrecovered material is separated with a Low Intensity Magnetite Separator (LIMS). In this separator two streams are produced: one stream contains magnetite and the other one is void of magnetite. The magnetite bearing stream is processed in the Magnetite Plant, which includes a series of ball mills, hydro-cyclones, and two additional stages of LIMS. The magnetite concentrate produced is pumped to the Pellet Plant. The non-magnetite

stream from the first stage of LIMS is further processed in the Hematite Plant, which consist in additional screens and spiral separators that recover hematite. The hematite concentrate is dewatered using horizontal vacuum filters and then conveyed to either concentrate stockpiles, train silos or to the Pellet Plant (IOC, 2008b).

The silica based waste, produced in the concentrators (Primary Spiral Plant, the Magnetite Plant and the Hematite Plant), is pumped to the mining tailing dump. It is from this mining tailing dump that the samples were taken for this research thesis.

Appendix 3. Statistical used concepts.

Mean: ($\bar{x}$) sum of the observations divided by the number (n) of observations (Taylor, 1997). For the purpose of this research, the observations are defined as the sample elemental concentrations determined through the chemical analysis.

$$\bar{x} = (X_1 + X_2 + \cdots X_n) / n$$

Standard deviation: (s) is the measure of the variability of individual members in the data set (Taylor, 1997). In this case the data set is composed by the determined elemental concentrations of the samples. The standard deviation is given by the following formula:

$$s = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x_i - \bar{x})^2}$$

Standard deviation of the mean: s ($\bar{x}$) is a measure of the variability of the mean of n samples (Lomax, 2007). The standard deviation of the mean was calculated by the following formula:

$$s(\bar{x}) = s / (n)^{1/2}$$

Relative standard deviation f the mean: (r.s.d) measures how close the data is to the mean. It is measured in terms of percent and was calculated by the following formula:

$$r.s.d = (\sigma/\bar{x})\ 100$$

Relative standard deviation of A/B (propagation of error through division): the relative standard deviation of A/B was calculated by the following formula (Harris, 2002)

$$(r.s.d.\ A/B)^2 = (r.s.d\ A)^2 + (r.s.d.\ B)^2$$

Standard deviation of the difference of the means (propagation of error through subtraction): the propagation of error through subtraction was calculated through the following formula (Harris, 2002)

$$(\text{SD A-B})^2 = (s(\bar{r})_A)^2 + (s(\bar{r})_B)^2$$

t-Test: known as Student's t-Test, is a common statistical analysis developed by William Sealy Gossett (Lomax, 2007). This test was selected due to the fact that it effectively compares the means of two set of data (A and B) in order to find out if they are statistically significant different (Lomax, 2007). This is done by calculating an experimental t value. For this, the standard deviation of an individual determination (for each set of data) is calculated. Then, the standard deviation of the mean of each set is calculated. Subsequently, the difference of the means and the standard deviation of the difference of the means (propagation of error through subtraction) are calculated. Finally, the t value can be calculated by dividing the difference of the means by the standard deviation of the difference of the means (propagation of error through a subtraction). This calculated t value is compared with a critical value or threshold, which for this test was 2.78 (4 degrees of freedom), a value commonly used in statistical t-Test at a 95% confidence level (H. Longerich, personal communication, February 2, 2009). If t-Tests results generate larger values than 2.78 then the means of the two compared groups are significantly different. Values, smaller than -2.78, are considered statistically significant as well.

Appendix 4. Acid digestion of tailing samples (complete data).

Element	LD	CV-O-A			LD	CV-0-A			LD	CV-O-B			L.D.	CV-O-B	LD	CV-1		
Li	0.75	1.13	1.09	1.33	0.13	0.98	0.94	1.16	0.75	2.29	1.13	0.93	0.06	1.04	0.75	1.13	1.29	1.33
Ti	3.16	44.5	49.6	53.2	0.67	72.8	58.6	64.6	3.16	75.8	72.9	72.9	n.d.	n.d.	3.16	205	193	199
V	0.16	7.15	6.78	6.58	0.05	7.73	8.29	8.30	0.16	10.4	10.8	10.3	n.d.	n.d.	0.16	18.8	18.9	19.5
Cr	1.80	69.4	61.4	55.9	0.54	3.96	2.61	3.67	1.80	329	337	339	n.d.	n.d.	1.80	439	438	451
Rb	0.34	1.19	0.55	0.89	0.07	1.40	1.84	0.81	0.34	1.07	0.69	0.45	0.19	0.49	0.34	<L.D.*	1.00	0.84
Sr	2.28	6.98	6.88	11.94	0.74	5.79	5.22	5.79	2.28	8.97	9.46	21.2	1.66	8.60	2.28	13.3	15.1	14.7
Y	0.14	4.30	4.00	3.90	0.07	4.05	3.93	4.00	0.14	3.87	3.98	4.16	0.07	3.64	0.14	6.48	6.56	6.88
Zr	0.33	4.08	4.21	4.36	0.09	6.25	5.79	5.02	0.33	5.53	5.42	5.03	0.25	4.97	0.33	6.52	6.75	8.73
Nb	0.19	1.74	1.62	1.62	0.06	1.57	1.81	1.59	0.19	2.27	2.26	2.10	0.14	1.89	0.19	2.86	2.79	2.99
Mo	1.09	2.27	<L.D.*	2.30	0.29	0.58	<L.D.*	0.32	1.09	4.36	3.45	3.22	0.85	2.97	1.09	3.93	4.82	6.28
Cs	0.11	<L.D.*	<L.D.*	<L.D.*	0.06	0.41	0.34	0.39	0.11	<L.D.*	<L.D.*	<L.D.*	0.06	<L.D.*	0.11	<L.D.*	<L.D.*	<L.D.*
Ba	1.46	8.61	8.09	18.15	2.02	7.29	6.76	11.19	1.46	15.0	13.3	14.0	0.60	11.76	1.46	17.8	18.6	19.0
La	0.10	1.90	1.85	3.09	0.02	1.80	2.04	1.61	0.10	2.01	2.08	2.43	0.03	2.24	0.10	3.92	3.86	3.95
Ce	0.11	4.15	4.01	5.88	0.04	3.61	4.30	3.47	0.11	3.59	3.55	4.09	0.04	3.92	0.11	6.79	6.71	6.64
Pr	0.07	0.45	0.46	0.70	0.02	0.40	0.40	0.35	0.07	0.45	0.51	0.59	0.02	0.52	0.07	0.84	0.87	0.87
Nd	0.69	2.04	1.89	2.96	0.16	1.59	1.50	1.48	0.69	2.02	2.12	2.23	0.39	2.22	0.69	3.27	3.63	3.43
Sm	0.32	0.52	0.50	0.73	0.13	0.33	0.25	0.22	0.32	0.47	0.41	0.46	0.18	0.48	0.32	0.63	0.76	0.79
Eu	0.11	0.21	0.19	0.22	0.04	0.15	0.13	0.11	0.11	0.17	0.16	0.17	0.06	0.19	0.11	0.25	0.27	0.29
Gd	0.23	0.58	0.54	0.60	0.12	0.54	0.45	0.49	0.23	0.51	0.51	0.54	0.12	0.52	0.23	0.79	0.84	0.80
Tb	0.05	0.10	0.09	0.10	0.01	0.08	0.06	0.06	0.05	0.08	0.08	0.09	0.02	0.08	0.05	0.12	0.13	0.14
Dy	0.18	0.69	0.59	0.62	0.06	0.54	0.49	0.50	0.18	0.57	0.58	0.61	0.08	0.57	0.18	0.88	0.95	0.97
Ho	0.04	0.14	0.14	0.14	0.02	0.14	0.11	0.11	0.04	0.12	0.13	0.13	0.02	0.12	0.04	0.20	0.21	0.21
Er	0.16	0.50	0.48	0.49	0.06	0.39	0.33	0.36	0.16	0.40	0.37	0.46	0.08	0.38	0.16	0.58	0.71	0.68
Tm	0.04	0.08	0.10	0.10	0.01	0.06	0.04	0.06	0.04	0.06	0.09	0.10	0.01	0.07	0.04	0.08	0.13	0.13
Yb	0.19	0.53	0.47	0.51	0.07	0.40	0.34	0.33	0.19	0.38	0.38	0.43	0.12	0.36	0.19	0.61	0.63	0.66
Lu	0.04	0.07	0.07	0.07	0.02	0.06	0.04	0.05	0.04	0.06	0.05	0.06	0.02	0.05	0.04	0.08	0.09	0.08
Hf	0.20	<L.D.*	<L.D.*	<L.D.*	0.11	0.14	<0.11	<0.11	0.20	<L.D.*	<L.D.*	<L.D.*	0.13	0.14	0.20	<L.D.*	<L.D.*	<L.D.*
Ta	0.04	1.61	1.62	1.56	0.03	1.53	1.63	1.60	0.04	<L.D.*	<L.D.*	<L.D.*	0.03	0.03	0.04	<L.D.*	<L.D.*	<L.D.*
Tl	0.20	<L.D.*	<L.D.*	<L.D.*	0.04	<L.D.*	<L.D.*	<L.D.*	0.20	<L.D.*	<L.D.*	<L.D.*	0.03	<L.D.*	0.20	<L.D.*	<L.D.*	<L.D.*
Pb	0.46	0.53	<L.D.*	1.61	1.88	<L.D.*	<L.D.*	<L.D.*	0.46	0.72	0.69	0.54	0.19	0.50	0.46	<L.D.*	0.54	0.70
Bi	0.07	<L.D.*	<L.D.*	0.08	0.02	<L.D.*	<L.D.*	<L.D.*	0.07	0.11	0.11	0.09	0.02	<L.D.*	0.07	<L.D.*	0.11	<L.D.*
Th	0.05	0.09	0.10	0.12	0.01	0.07	0.10	0.05	0.05	0.08	0.07	0.11	0.02	0.12	0.05	0.21	0.20	0.21
U	0.05	0.07	0.09	0.11	0.01	0.06	0.05	0.06	0.05	<L.D.*	<L.D.*	<L.D.*	0.02	0.03	0.05	<L.D.*	0.08	0.07

*Values below the limit of detection of the instrument. Note that concentration unit are ppm and elements that were not determined show n.d.

Appendix 4. (continued).

Element	L.D.	CV-1	CV-1	LD	CV-5			L.D.	CV-5	LD	CV-10			L.D.	CV-10
Li	0.06	2.44	1.50	0.75	1.09	0.81	<L.D.*	0.06	0.87	0.75	0.80	1.23	1.02	0.06	1.02
Ti				3.16	205	197	183			3.16	113	131	138		
V				0.16	16.8	17.9	14.8			0.16	10.5	12.6	13.63		
Cr				1.80	279	288	269			1.80	231	260	309		
Rb	0.19	0.96	0.88	0.34		0.95	0.70	0.19	0.97	0.34	1.42	1.12	0.92	0.19	1.16
Sr	1.66	14.1	14.1	2.28	12.6	12.3	11.8	1.66	13.1	2.28	10.6	11.2	11.5	1.66	12.0
Y	0.07	6.30	6.46	0.14	6.55	6.34	6.14	0.07	6.76	0.14	5.44	5.48	5.40	0.07	5.95
Zr	0.25			0.33	5.33	5.15	4.18	0.25	5.88	0.33	3.76	5.43	4.42	0.25	4.68
Nb	0.14	2.30	2.30	0.19	1.88	1.78	1.49	0.14	1.79	0.19	1.36	1.51	1.56	0.14	1.61
Mo	0.85	3.84	3.73	1.09	4.24	4.17	4.89	0.85	3.88	1.09	2.31	2.63	2.56	0.85	3.55
Cs	0.06	<L.D.*	<L.D.*	0.11	<L.D.*	<L.D.*	<L.D.*	0.06	<L.D.*	0.11	<L.D.*	<L.D.*	<L.D.*	0.06	<L.D.*
Ba	0.60	18.0	18.2	1.46	17.6	24.4	17.9	0.60	18.8	1.46	16.05	17.09	17.7	0.60	19.44
La	0.03	3.73	3.83	0.10	3.28	3.13	3.56	0.03	3.63	0.10	2.63	2.73	2.92	0.03	3.30
Ce	0.04	6.40	6.72	0.11	5.32	5.06	5.63	0.04	6.04	0.11	4.87	4.91	5.19	0.04	5.90
Pr	0.02	0.83	0.87	0.07	0.73	0.75	0.79	0.02	0.78	0.07	0.60	0.65	0.68	0.02	0.76
Nd	0.39	3.36	3.32	0.69	3.34	3.18	3.11	0.39	3.30	0.69	2.57	2.57	2.64	0.39	3.14
Sm	0.18	0.73	0.68	0.32	0.81	0.66	0.61	0.18	0.68	0.32	0.55	0.56	0.51	0.18	0.66
Eu	0.06	0.26	0.25	0.11	0.29	0.23	0.22	0.06	0.28	0.11	0.22	0.20	0.19	0.06	0.26
Gd	0.12	0.80	0.77	0.23	0.81	0.75	0.73	0.12	0.85	0.23	0.76	0.72	0.69	0.12	0.77
Tb	0.02	0.13	0.12	0.05	0.17	0.13	0.11	0.02	0.14	0.05	0.11	0.10	0.10	0.02	0.12
Dy	0.08	0.87	0.93	0.18	0.94	0.83	0.84	0.08	0.98	0.18	0.83	0.78	0.76	0.08	0.90
Ho	0.02	0.26	0.20	0.04	0.22	0.20	0.19	0.02	0.21	0.04	0.18	0.17	0.16	0.02	0.20
Er	0.08	0.66	0.65	0.16	0.71	0.63	0.59	0.08	0.69	0.16	0.54	0.54	0.56	0.08	0.63
Tm	0.01	0.11	0.12	0.04	0.11	0.13	0.12	0.01	0.09	0.04	0.08	0.12	0.11	0.01	0.11
Yb	0.12	0.62	0.64	0.19	0.70	0.61	0.58	0.12	0.64	0.19	0.55	0.53	0.48	0.12	0.59
Lu	0.02	0.08	0.08	0.04	0.09	0.08	0.08	0.02	0.09	0.04	0.08	0.07	0.07	0.02	0.07
Hf	0.13	0.57	0.43	0.20	<L.D.*	<L.D.*	<L.D.*	0.13	0.76	0.20	<L.D.*	<L.D.*	<L.D.*	0.13	0.30
Ta	0.03	0.05	0.04	0.04	0.05	<L.D.*	<L.D.*	0.03	0.03	0.04	<L.D.*	<L.D.*	<L.D.*	0.03	<L.D.*
Tl	0.03	0.04	0.04	0.20	<L.D.*	<L.D.*	<L.D.*	0.03	<0.032	0.20	<L.D.*	<L.D.*	<L.D.*	0.03	<L.D.*
Pb	0.19	0.52	0.72	0.46	<L.D.*	<L.D.*	<L.D.*	0.19	0.40	0.46	<L.D.*	<L.D.*	<L.D.*	0.19	0.46
Bi	0.02	0.03	0.04	0.07	0.17	0.11	0.12	0.02	<0.019	0.07	<L.D.*	<L.D.*	<L.D.*	0.02	<L.D.*
Th	0.02	0.26	0.22	0.05	0.15	0.09	0.09	0.02	0.14	0.05	<L.D.*	0.13	0.08	0.02	0.11
U	0.02	0.09	0.11	0.05	0.07	0.08	0.08	0.02	0.04	0.05	<L.D.*	0.06	0.05	0.02	0.05

*Values below the limit of detection of the instrument. Note that concentration unit are ppm and elements that were not determined show n.d.

Appendix 5. Primitive Mantle composition.

Element	(ppm)
Th	0.085
Nb	0.713
La	0.687
Ce	1.78
Pr	0.276
Nd	1.35
Zr	11.2
Sm	0.444
Eu	0.168
Gd	0.596
Dy	0.737
Ho	0.164
Y	4.55
Er	0.48
Yb	0.493
Lu	0.074
Ti	1300
V	82
Cr	2940
Sr	21.100
Rb	0.635

(Rollinson, 1993)

Appendix 6. Complete data for length of digestion experiments.

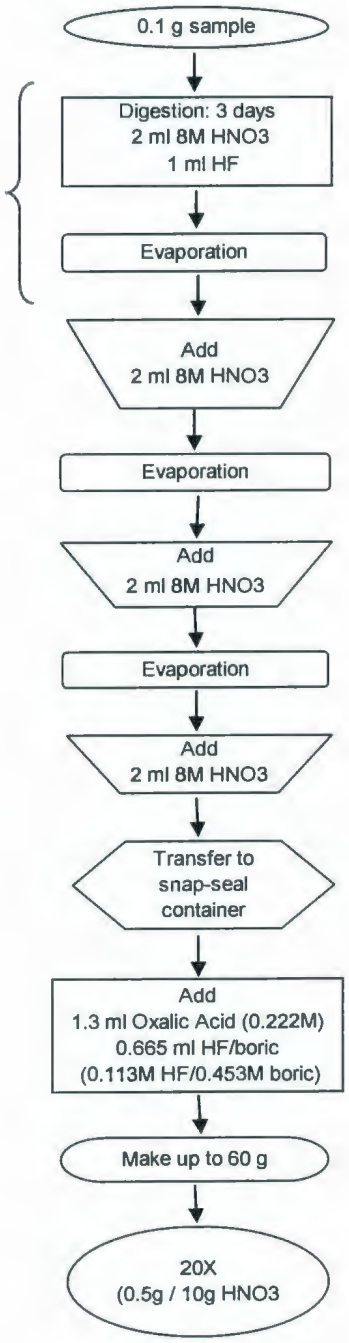
Element	L.D.	1 day digestion		2 day digestion		3 day digestion		4 day digestion		5 day digestion		6 day digestion		7 day digestion	
Li	0.30	31.7	31.3	32.4	30.6	30.4	29.0	30.6	28.6	31.0	31.4	31.6	29.0	31.9	30.2
Rb	0.47	170	183	159	169	142	141	157	144	171	177	175	142	158	160
Sr	2.65	495	536	473	489	415	419	461	405	489	491	481	393	452	459
Y	0.25	8.29	9.13	7.59	8.34	6.98	6.98	7.72	6.83	7.81	8.19	8.07	6.46	7.51	7.50
Zr	0.67	39.1	39.1	38.1	39.9	36.3	35.8	35.4	34.5	39.3	47.0	47.8	40.0	44.0	43.4
Nb	0.44	13.6	14.2	13.0	13.4	12.3	12.2	12.9	11.9	13.6	13.7	13.7	12.0	13.5	13.4
Mo	2.64	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.
Cs	0.17	1.59	1.49	1.43	1.47	1.43	1.33	1.34	1.28	1.40	1.36	1.38	1.26	1.29	1.32
Ba	1.64	2423	2583	2417	2467	2265	2199	2360	2155	2426	2496	2442	2192	2473	2399
La	0.14	89.6	94.0	88.6	90.0	82.5	81.1	86.2	79.2	89.2	91.7	89.4	81.1	90.7	88.2
Ce	0.14	174	183	168	164	152	147	162	145	164	168	164	148	159	153
Pr	0.12	17.2	17.6	16.4	17.1	15.8	15.3	16.4	15.0	16.8	17.2	16.8	15.4	17.1	16.3
Nd	1.86	54.2	57.5	52.2	54.2	49.3	48.3	52.5	47.2	53.1	54.4	52.6	47.3	53.5	51.3
Sm	0.91	7.47	7.78	7.10	7.02	6.59	6.44	6.76	6.28	6.77	6.81	6.87	6.03	6.63	6.48
Eu	0.32	1.50	1.53	1.38	1.44	1.30	1.24	1.31	1.17	1.27	1.28	1.24	1.09	1.23	1.20
Gd	0.63	3.09	3.29	2.79	3.05	2.86	2.72	2.84	2.59	2.74	2.75	2.68	2.46	3.00	2.91
Tb	0.12	0.41	0.41	0.36	0.35	0.31	0.30	0.32	0.31	0.31	0.30	0.29	0.26	0.27	0.27
Dy	0.51	2.19	2.24	2.04	2.09	1.81	1.76	1.96	1.82	1.82	1.81	1.87	1.63	1.77	1.64
Ho	0.11	0.36	0.35	0.31	0.31	0.27	0.26	0.28	0.25	0.25	0.26	0.26	0.23	0.24	0.23
Er	0.47	0.94	0.89	0.78	0.69	0.73	0.63	0.58	0.60	0.58	0.50	0.58	0.46	0.45	0.44
Tm	0.08	0.09	0.10	0.08	<L.D.	0.12	0.11	<L.D.	0.09	0.13	<L.D.	0.10	0.11	<L.D.	<L.D.
Yb	0.69	0.73	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.
Lu	0.13	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.
Hf	0.81	1.56	1.24	1.11	1.22	0.93	0.82	0.84	<L.D.	<L.D.	0.96	0.95	<0.81	0.96	0.83
Ta	0.16	0.92	0.93	0.88	0.91	0.84	0.82	0.81	0.79	0.82	0.84	0.86	0.77	0.93	0.87
Tl	0.16	0.97	0.96	0.91	0.85	0.91	0.86	0.80	0.84	0.89	0.76	0.90	0.85	0.79	0.85
Pb	0.58	31.3	30.1	30.7	29.5	29.0	28.3	29.6	28.0	29.7	30.7	30.2	28.6	31.1	29.2
Bi	0.16	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.	<L.D.
Th	0.17	24.8	24.4	24.3	25.1	23.8	23.0	25.6	24.0	25.1	26.4	26.4	24.3	25.7	24.1
U	0.10	1.79	1.79	1.62	1.63	1.59	1.67	1.55	1.59	1.95	1.86	1.82	1.58	1.74	1.64

*Values below the limit of detection of the instrument.

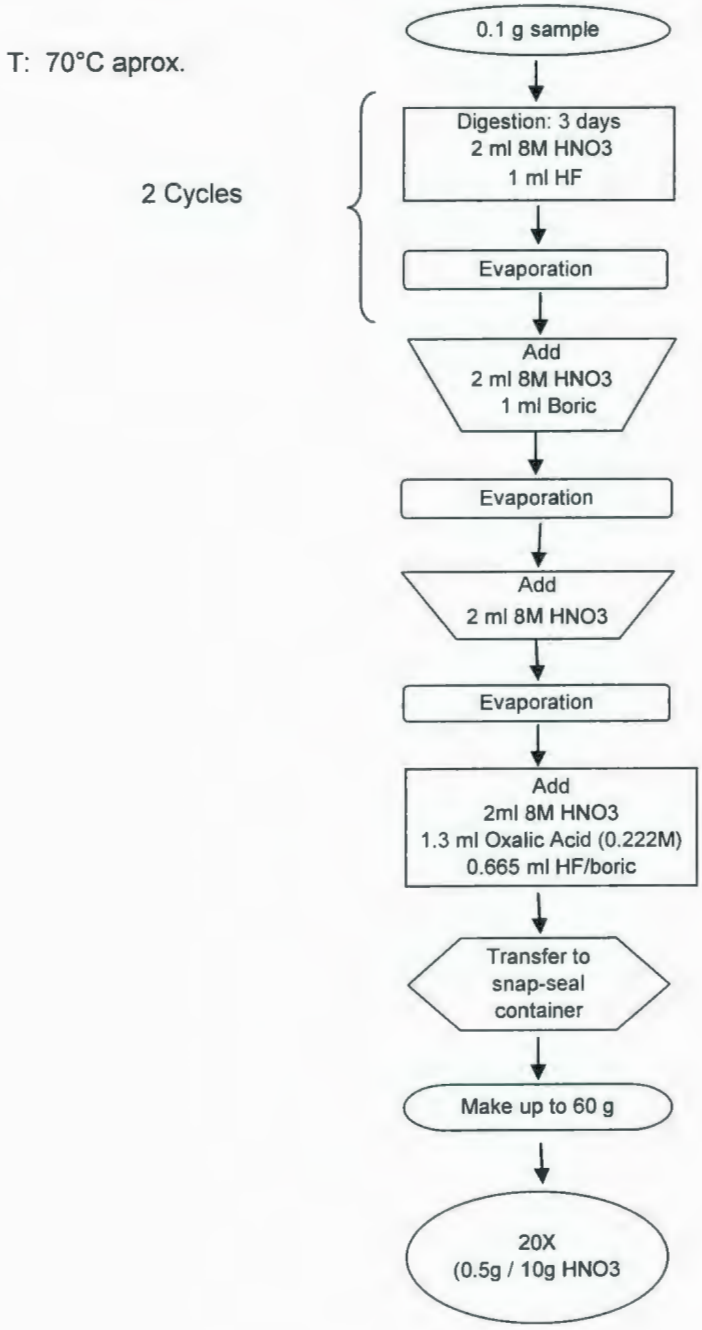
Appendix 7. Trial 1 (T1) – No H_3BO_3.

T: 70°C aprox.

2 Cycles



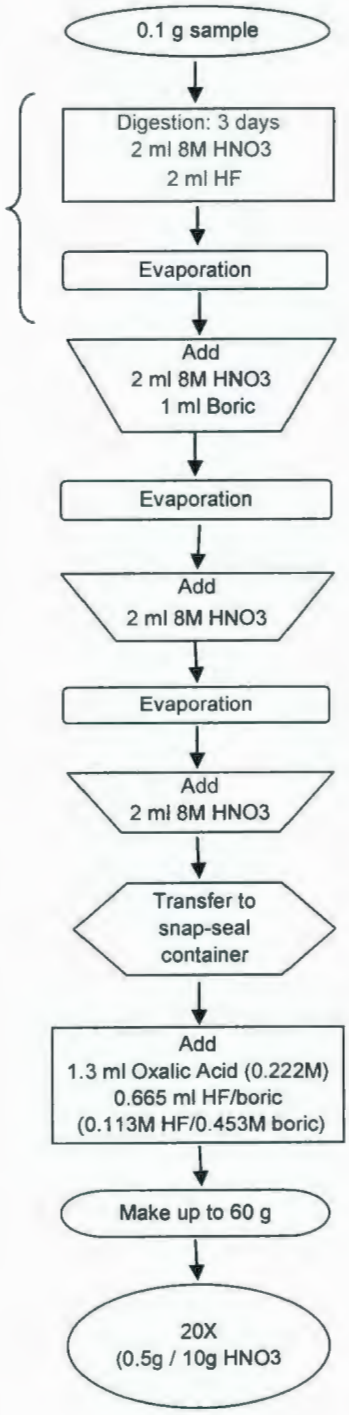
Appendix 8. Trial 2 (T2) – Heating $H_2C_2O_4$+HF/ H_3BO_3 mixture.



Appendix 9. Trail 3 (T3) - 2 mL of HF.

T: 70°C aprox.

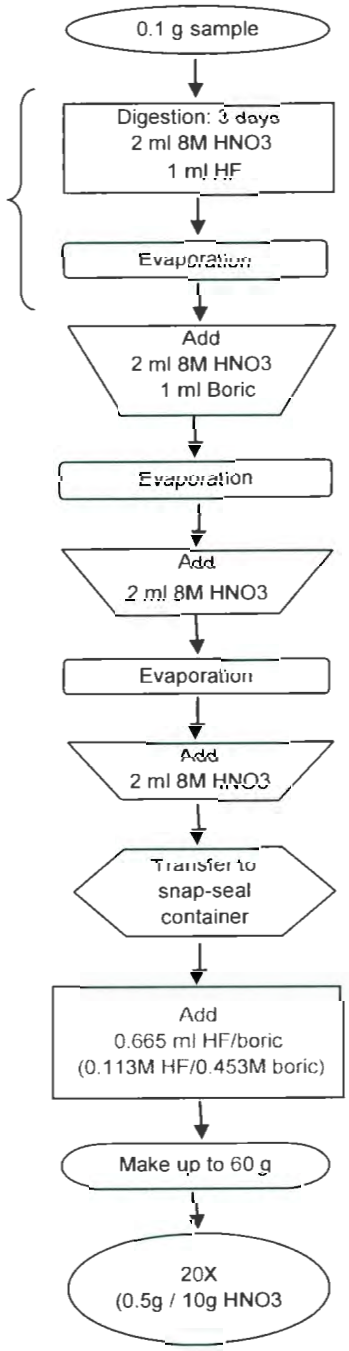
2 Cycles



Appendix 10. Trial 4 (T4) - No $H_2C_2O_4$.

T: 70°C aprox.

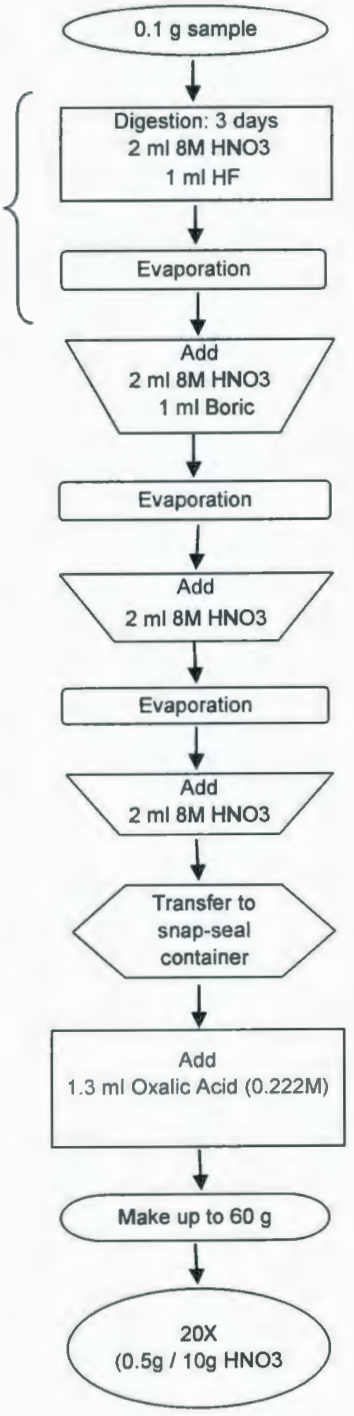
2 Cycles



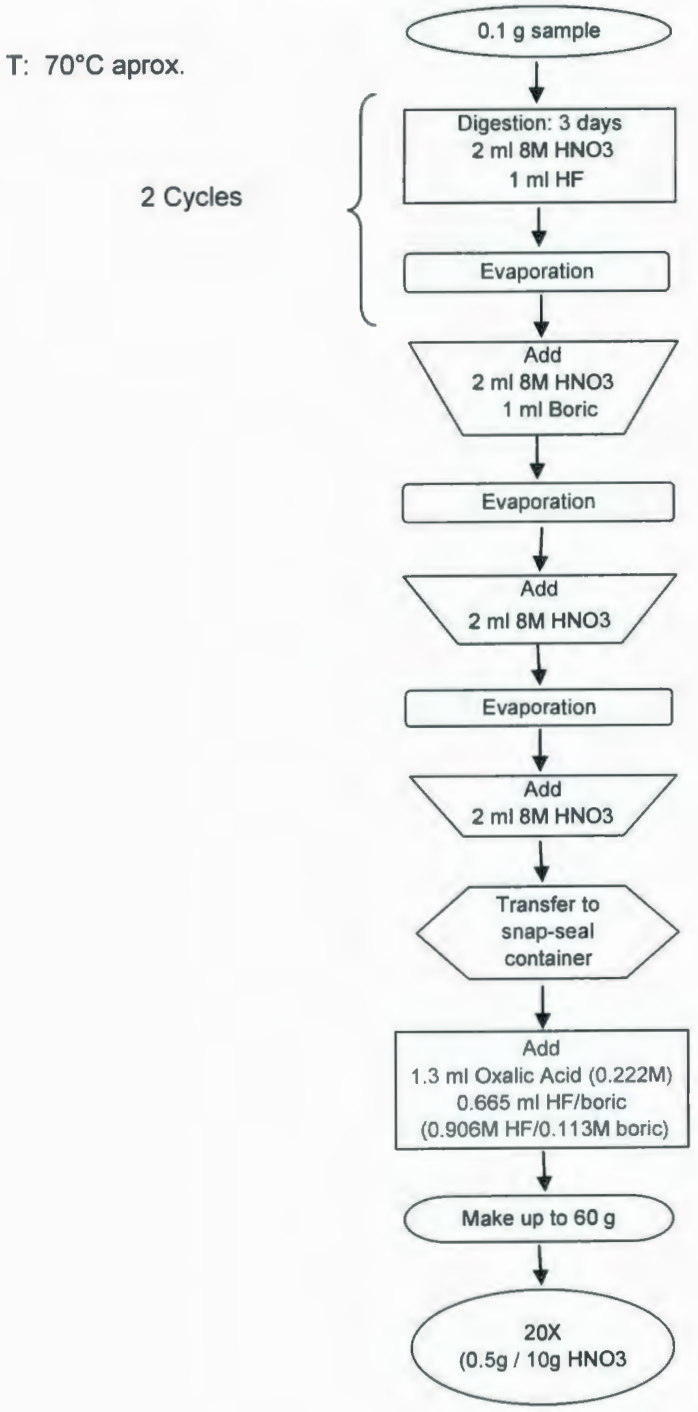
Appendix 11. Trial 5 (T5) - No HF/H_3BO_3.

T: 70°C aprox.

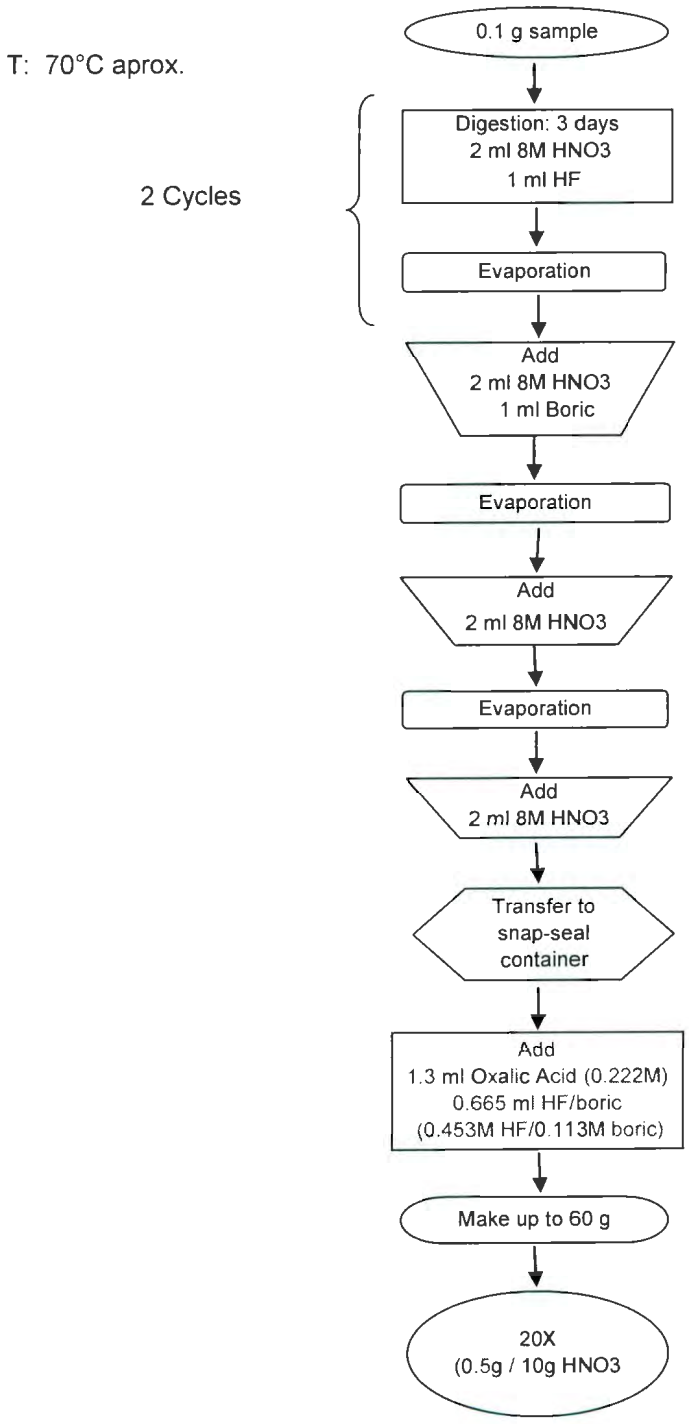
2 Cycles



Appendix 12. Trial 6 (T6) – Different concentration HF/ H_3BO_3 mixture (a).



Appendix 13. Trial 7 (T7) - Different concentration HF/H_3BO_3 mixture (b).



Appendix 14. First set of experiments (TO, T1, T2, T3 and T4).

Element	L.D.	TO			T1			T2			T3			T4
Li	0.13	0.98	0.94	1.16	1.37	1.00	0.99	1.10	1.09	1.05	1.03	0.97	0.99	1.03
Ti	0.67	72.8	58.6	64.6	50.8	54.2	53.0	59.9	71.7	65.1	64.4	52.2	87.1	51.5
V	0.05	7.73	8.29	8.30	8.10	8.05	7.72	8.06	8.83	8.48	8.73	8.32	7.71	7.61
Cr	0.54	3.96	2.61	3.67	2.60	3.94	3.09	4.55	4.42	4.07	5.95	4.26	3.91	3.10
Rb	0.07	1.40	1.84	0.81	0.41	1.06	0.54	0.54	2.77	0.56	0.45	1.53	0.54	0.41
Sr	0.74	5.79	5.22	5.79	6.32	6.13	5.71	5.72	17.0	6.64	6.00	6.26	5.74	6.13
Y	0.07	4.05	3.93	4.00	4.26	4.17	3.95	4.12	4.28	4.35	4.24	4.26	4.45	4.09
Zr	0.09	6.25	5.79	5.02	5.02	5.83	5.24	5.40	5.78	5.85	5.30	5.58	14.96	4.88
Nb	0.06	1.57	1.81	1.59	1.54	1.62	1.56	1.56	1.63	1.63	1.65	1.70	1.65	1.51
Mo	0.29	0.58	L.D.*	0.32	L.D.*	0.41	0.50	0.64	0.61	0.63	0.41	0.67	0.50	0.47
Cs	0.06	0.41	0.34	0.39	0.19	0.17	0.21	0.47	0.49	0.33	0.37	0.43	0.31	0.32
Ba	2.02	7.29	6.76	11.19	8.57	9.48	8.16	8.46	20.3	38.62	9.41	8.43	6.99	8.14
La	0.02	1.80	2.04	1.61	2.01	2.55	1.73	1.85	2.04	2.48	1.80	1.80	2.02	1.94
Ce	0.04	3.61	4.30	3.47	3.80	4.62	3.84	3.77	4.07	4.51	3.77	3.73	3.83	3.81
Pr	0.02	0.40	0.40	0.35	0.47	0.52	0.41	0.44	0.46	0.56	0.43	0.39	0.44	0.45
Nd	0.16	1.59	1.50	1.48	1.70	2.14	1.75	1.78	1.92	2.22	1.72	1.61	1.78	1.88
Sm	0.13	0.33	0.25	0.22	0.37	0.45	0.39	0.41	0.41	0.45	0.39	0.40	0.43	0.39
Eu	0.04	0.15	0.13	0.11	0.13	0.17	0.15	0.16	0.17	0.20	0.16	0.17	0.16	0.16
Gd	0.12	0.54	0.45	0.49	0.50	0.60	0.56	0.58	0.57	0.62	0.58	0.56	0.55	0.57
Tb	0.01	0.08	0.06	0.06	0.07	0.08	0.08	0.07	0.07	0.08	0.08	0.08	0.08	0.08
Dy	0.06	0.54	0.49	0.50	0.51	0.56	0.50	0.57	0.59	0.58	0.55	0.55	0.57	0.55
Ho	0.02	0.14	0.11	0.11	0.12	0.13	0.13	0.13	0.14	0.14	0.13	0.13	0.14	0.13
Er	0.06	0.39	0.33	0.36	0.44	0.40	0.40	0.43	0.44	0.44	0.43	0.44	0.45	0.44
Tm	0.01	0.06	0.04	0.06	0.08	0.06	0.07	0.09	0.06	0.08	0.08	0.07	0.09	0.09
Yb	0.07	0.40	0.34	0.33	0.39	0.44	0.38	0.43	0.42	0.43	0.45	0.48	0.49	0.42
Lu	0.02	0.06	0.04	0.05	0.04	0.07	0.06	0.07	0.07	0.07	0.07	0.07	0.09	0.07
Hf	0.11	0.14	0.09	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	0.16	L.D.*	L.D.*	0.11	0.34	0.04
Ta	0.03	1.53	1.63	1.60	1.58	1.59	1.56	1.63	1.63	1.72	1.61	1.48	1.51	1.50
Tl	0.04	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	0.04
Pb	1.88	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*
Bi	0.02	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	L.D.*	0.04	0.04	L.D.*	0.03	0.03
Th	0.01	0.07	0.10	0.05	0.05	0.08	0.05	0.07	0.09	0.08	0.06	0.06	0.14	0.06
U	0.01	0.06	0.05	0.06	0.08	0.06	0.08	0.08	0.07	0.08	0.08	0.08	0.12	0.09

*Values below the limit of detection of the instrument.

Appendix 15. First set of experiments (T4, T5, T6, T7 and T8).

Element	L.D.	T4		T5			T6			T7			T8	
Li	0.34	1.30	1.21	21.56	1.09	1.17	1.02	1.08	1.11	1.77	1.22	1.06	0.98	1.09
Ti	4.73	55.7	55.4	61.4	47.0	50.6	42.5	50.6	70.9	64.4	55.5	49.4	48.4	58.0
V	0.23	9.2	8.6	7.6	6.8	7.7	6.6	7.5	7.5	9.0	8.6	7.2	7.3	8.4
Cr	1.47	4.3	3.9	4.2	3.4	4.6	3.1	3.1	2.8	5.6	4.0	3.3	4.4	4.8
Rb	0.56	1.97	0.80	0.65	1.12	0.72	0.43	1.05	<L.D.*	0.63	1.14	<L.D.*	<L.D.*	<L.D.*
Sr	2.02	7.70	7.35	6.81	6.08	6.94	5.84	6.76	6.11	7.90	7.31	6.54	5.75	6.28
Y	0.15	4.88	4.65	4.02	3.79	4.31	3.71	4.08	4.08	4.97	4.78	4.09	3.93	4.67
Zr	0.41	6.41	5.48	5.97	4.69	5.29	5.68	6.52	6.19	6.64	6.10	4.61	4.96	9.68
Nb	0.30	1.90	1.83	1.77	1.61	1.79	1.53	1.77	1.69	2.08	2.07	1.66	1.58	1.71
Mo	1.53	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Cs	0.25	0.36	0.30	0.26	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Ba	2.02	10.1	9.9	10.3	7.9	10.1	10.1	8.9	7.5	6.9	9.3	7.4	8.8	9.5
La	0.21	2.47	2.00	2.16	1.73	2.27	1.72	1.77	1.92	2.05	2.00	2.01	1.73	2.19
Ce	0.12	4.6	4.0	4.0	3.5	4.3	3.6	4.0	3.9	4.3	4.3	4.0	3.5	4.1
Pr	0.10	0.53	0.50	0.47	0.41	0.52	0.41	0.42	0.45	0.51	0.46	0.48	0.43	0.54
Nd	1.17	2.54	2.19	2.02	1.89	2.32	1.80	2.01	1.91	2.29	2.20	1.91	1.60	2.22
Sm	0.63	0.68	<L.D.*	<L.D.*	<L.D.*	0.73	<L.D.*	<L.D.*	<L.D.*	0.76	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Eu	0.18	0.24	0.21	0.21	0.22	0.24	<L.D.*	<L.D.*	<L.D.*	0.25	0.23	0.20	<L.D.*	<L.D.*
Gd	0.37	0.77	0.70	0.64	0.59	0.70	0.53	0.50	0.48	0.70	0.67	0.58	0.54	0.55
Tb	0.07	0.11	0.10	0.10	0.10	0.11	0.09	0.08	0.10	0.11	0.10	0.08	0.08	0.08
Dy	0.25	0.70	0.65	0.65	0.62	0.67	0.51	0.58	0.53	0.75	0.72	0.57	0.61	0.68
Ho	0.06	0.17	0.16	0.14	0.14	0.15	0.12	0.14	0.12	0.17	0.17	0.13	0.15	0.14
Er	0.23	0.59	0.54	0.52	0.49	0.57	0.42	0.46	0.47	0.58	0.56	0.49	0.48	0.62
Tm	0.05	0.09	0.10	0.10	0.08	0.10	0.09	0.07	0.09	0.12	0.09	0.09	0.09	0.13
Yb	0.32	0.59	0.54	0.51	0.48	0.54	0.42	0.49	0.40	0.60	0.57	0.45	0.51	0.52
Lu	0.07	0.10	0.09	0.10	0.08	0.09	0.07	<L.D.*	0.07	0.10	0.09	0.07	0.07	<L.D.*
Hf	0.29	0.29	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Ta	0.06	1.74	1.57	1.56	1.37	1.49	1.42	1.54	1.47	1.80	1.78	1.49	1.54	1.62
Tl	0.12	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Pb	0.40	0.54	0.54	0.62	<L.D.*	0.73	0.46	<L.D.*	0.41	0.63	0.60	<L.D.*	<L.D.*	0.43
Bi	0.08	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Th	0.07	0.12	0.07	0.08	0.08	0.10	0.07	0.08	<L.D.*	0.08	0.08	<L.D.*	<L.D.*	0.08
U	0.07	0.08	0.09	0.10	0.07	0.11	0.08	0.05	0.09	0.11	0.08	0.08	0.07	0.11

*Values below the limit of detection of the instrument.

Appendix 16. First set of experiments (T0 10X, T1 10X, T2 10X, and T3 10X).

Element	L.D.	T0 10X			T1 10X			T2 10X			T3 10X
Li	0.34	0.76	0.61	0.78	1.50	1.22	1.26	1.50	1.37	1.27	1.25
Ti	4.73	77.1	52.7	57.7	39.7	47.2	51.5	55.1	60.0	54.6	53.2
V	0.23	8.33	8.21	8.04	6.19	7.21	7.35	7.35	7.36	6.96	7.15
Cr	1.47	3.52	2.31	3.00	2.16	3.07	2.58	3.51	3.37	2.75	4.30
Rb	0.56	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Sr	2.02	4.71	2.81	3.47	6.61	6.18	6.51	6.04	17.29	6.28	6.05
Y	0.15	4.29	4.03	3.97	3.85	4.12	4.22	4.12	4.32	4.27	4.12
Zr	0.41	5.87	4.93	4.97	4.61	4.79	5.46	5.35	5.20	5.60	4.87
Nb	0.30	1.59	1.83	1.52	1.64	1.81	1.88	1.78	1.85	1.81	1.87
Mo	1.53	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Cs	0.25	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Ba	2.02	5.50	4.13	9.69	12.12	8.68	8.98	8.81	21.00	7.79	9.05
La	0.21	1.90	1.96	1.55	1.95	2.53	1.87	1.91	2.00	2.45	1.82
Ce	0.12	3.93	4.59	3.69	3.81	4.81	4.31	3.97	4.50	4.88	4.23
Pr	0.10	0.31	0.29	0.27	0.52	0.54	0.44	0.48	0.46	0.56	0.44
Nd	1.17	<L.D.*	<L.D.*	<L.D.*	1.90	2.15	1.90	1.75	1.92	2.30	1.80
Sm	0.63	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Eu	0.18	<L.D.*	<L.D.*	<L.D.*	<L.D.*	0.18	0.18	<L.D.*	0.19	0.19	<L.D.*
Gd	0.37	<L.D.*	<L.D.*	<L.D.*	0.52	0.61	0.52	0.52	0.56	0.58	0.54
Tb	0.07	<L.D.*	<L.D.*	<L.D.*	0.07	0.09	0.08	0.08	0.09	0.08	0.10
Dy	0.25	<L.D.*	<L.D.*	<L.D.*	0.54	0.64	0.61	0.59	0.61	0.63	0.62
Ho	0.06	<L.D.*	<L.D.*	<L.D.*	0.12	0.14	0.14	0.13	0.14	0.14	0.13
Er	0.23	<L.D.*	<L.D.*	<L.D.*	0.50	0.42	0.49	0.45	0.44	0.45	0.47
Tm	0.05	<L.D.*	<L.D.*	<L.D.*	0.16	0.07	0.08	0.10	0.07	0.09	0.09
Yb	0.32	<L.D.*	<L.D.*	<L.D.*	0.41	0.41	0.44	0.38	0.41	0.45	0.46
Lu	0.07	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	0.07	<L.D.*	<L.D.*	<L.D.*	0.07
Hf	0.29	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Ta	0.06	1.54	1.48	1.44	1.32	1.53	1.58	1.92	1.84	1.88	1.85
Tl	0.12	<L.D.*	<L.D.*	<L.D.*	0.14	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Pb	0.40	<L.D.*	<L.D.*	<L.D.*	0.78	<L.D.*	<L.D.*	0.72	0.56	<L.D.*	<L.D.*
Bi	0.08	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Th	0.07	<L.D.*	<L.D.*	<L.D.*	<L.D.*	0.07	<L.D.*	<L.D.*	0.07	0.08	0.07
U	0.07	<L.D.*	<L.D.*	<L.D.*	0.15	0.07	0.08	0.11	<L.D.*	0.08	0.08

*Values below the limit of detection of the instrument.

Appendix 17. First set of experiments (T3, T3, T3 10X, T4 10X, T5 10X).

Element	L.D.	T3	T8	T3 10X		T4 10X			T5 10X		
Li	5.04	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*
Ti	2.98	81.9	51.7	43.6	83.8	48.2	44.1	48.3	53.6	43.3	42.4
V	0.22	7.43	8.04	7.13	7.34	7.27	7.44	7.53	6.77	6.35	6.79
Cr	2.32	60.3	176	63.7	77.3	91.6	103	117	105	98.9	114
Rb	4.20	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*
Sr	1.84	4.81	6.03	5.30	5.46	5.10	5.33	5.49	5.78	5.30	5.62
Y	0.17	4.43	4.23	3.99	4.55	3.86	3.87	4.03	4.09	3.75	4.07
Zr	0.39	17.4	6.32	4.96	15.1	4.71	4.40	4.58	6.21	4.60	4.85
Nb	0.21	1.84	1.89	1.73	1.89	1.58	1.58	1.68	1.88	1.66	1.74
Mo	1.25	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*
Cs	0.54	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*
Ba	2.16	6.11	11.0	8.05	7.31	7.69	8.07	8.84	10.1	15.9	8.92
La	0.13	1.97	1.99	1.72	2.07	1.87	1.98	1.75	2.13	1.80	2.20
Ce	0.12	4.35	4.30	3.83	4.32	4.02	4.01	3.92	4.74	4.04	4.68
Pr	0.10	0.35	0.43	0.36	0.42	0.39	0.40	0.38	0.39	0.42	0.43
Nd	1.22	<L.D*	2.04	<L.D*	1.39	1.46	1.31	1.37	1.40	1.47	1.69
Sm	0.63	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*
Eu	0.18	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*
Gd	0.43	<L.D*	0.53	<L.D*	<L.D*	<L.D*	<L.D*	0.44	<L.D*	<L.D*	<L.D*
Tb	0.08	<L.D*	0.09	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	0.08
Dy	0.32	<L.D*	0.55	0.43	0.54	0.49	0.47	0.49	0.47	0.42	0.51
Ho	0.08	0.10	0.14	0.10	0.12	0.10	0.10	0.11	0.12	0.11	0.11
Er	0.34	<L.D*	0.47	0.35	0.41	<L.D*	0.34	<L.D*	0.36	0.36	0.37
Tm	0.07	<L.D*	0.10	<L.D*	0.07	<L.D*	<L.D*	<L.D*	<L.D*	0.08	<L.D*
Yb	0.44	<L.D*	0.46	<L.D*	0.35	0.27	0.31	0.22	0.27	0.26	0.30
Lu	0.07	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*
Hf	0.37	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*
Ta	0.07	1.56	1.88	1.33	1.60	1.43	1.45	1.44	1.50	1.35	1.47
Tl	0.11	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*
Pb	0.23	0.28	0.48	0.26	<L.D*	0.45	0.24	0.40	0.29	0.32	<L.D*
Bi	0.09	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	0.19	<L.D*	<L.D*
Th	0.08	0.09	<L.D*	<L.D*	0.11	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*	<L.D*
U	0.06	0.06	0.07	0.06	0.09	<L.D*	0.06	0.06	<L.D*	0.06	0.06

*Values below the limit of detection of the instrument.

Appendix 18: First set of experiments (T6 10X, T7 10X, T8 10X)

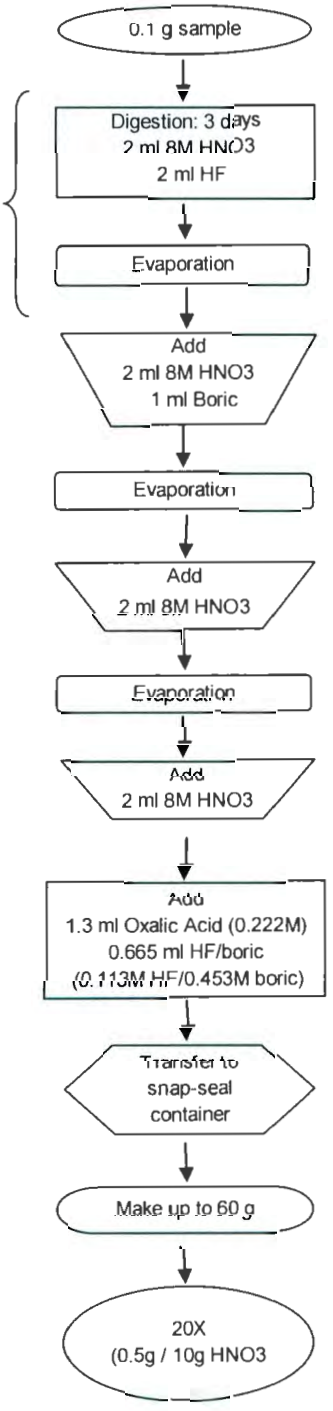
Element	L.D.	T6 10X			T7 10X			T8 10X		
Li	5.04	2.25	1.72	1.90	2.83	1.40	1.07	0.88	0.60	<L.D.*
Ti	2.98	46.1	51.9	75.8	53.7	48.3	51.6	53.6	54.9	55.8
V	0.22	6.98	7.90	7.91	7.47	7.47	7.73	7.76	7.83	8.53
Cr	2.32	150	198	201	138	140	143	196	160	220
Rb	4.20	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Sr	1.84	5.47	5.86	5.53	5.65	6.09	5.81	6.64	6.26	6.53
Y	0.17	3.90	4.00	4.00	3.99	3.87	4.04	4.24	4.46	4.45
Zr	0.39	5.69	5.55	5.27	5.76	4.73	4.23	5.37	8.66	6.47
Nb	0.21	1.78	1.79	1.80	1.80	1.75	1.72	1.82	1.87	1.93
Mo	1.25	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Cs	0.54	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Ba	2.16	10.3	7.56	8.01	9.24	7.45	7.56	9.83	8.91	11.2
La	0.13	1.77	1.77	1.85	1.66	1.66	1.99	1.88	1.93	2.12
Ce	0.12	4.17	4.06	4.12	3.77	3.71	4.22	4.15	4.14	4.39
Pr	0.10	0.38	0.38	0.39	0.36	0.38	0.42	0.43	0.40	0.50
Nd	1.22	1.33	1.53	1.50	1.25	1.37	1.70	1.74	1.69	2.17
Sm	0.63	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Eu	0.18	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	0.22
Gd	0.43	0.46	<L.D.*	<L.D.*	<L.D.*	<L.D.*	0.44	0.53	0.50	0.64
Tb	0.08	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	0.09	0.08	0.12
Dy	0.32	0.46	0.47	0.44	0.51	0.49	0.51	0.58	0.55	0.70
Ho	0.08	0.11	0.11	0.09	0.12	0.11	0.12	0.13	0.14	0.15
Er	0.34	<L.D.*	0.39	0.36	0.34	0.37	0.39	0.41	0.42	0.55
Tm	0.07	<L.D.*	0.05	0.05	0.04	0.06	0.07	0.08	0.06	0.12
Yb	0.44	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	0.50	0.49
Lu	0.07	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	0.07
Hf	0.37	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Ta	0.07	1.72	1.75	1.70	1.73	1.73	1.70	1.96	1.98	2.24
Tl	0.11	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Pb	0.23	0.24	0.27	0.52	0.25	0.30	0.24	0.38	0.40	0.46
Bi	0.09	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	0.22	<L.D.*	<L.D.*
Th	0.08	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	0.08
U	0.06	<L.D.*	0.06	0.06	0.04	0.06	<L.D.*	0.07	0.06	0.10

*Values below the limit of detection of the instrument.

Appendix 19. Trial 9 (T9) -1 mL HF, heating $H_2C_2O_4$, 8:1 HF/ H_3BO_3.

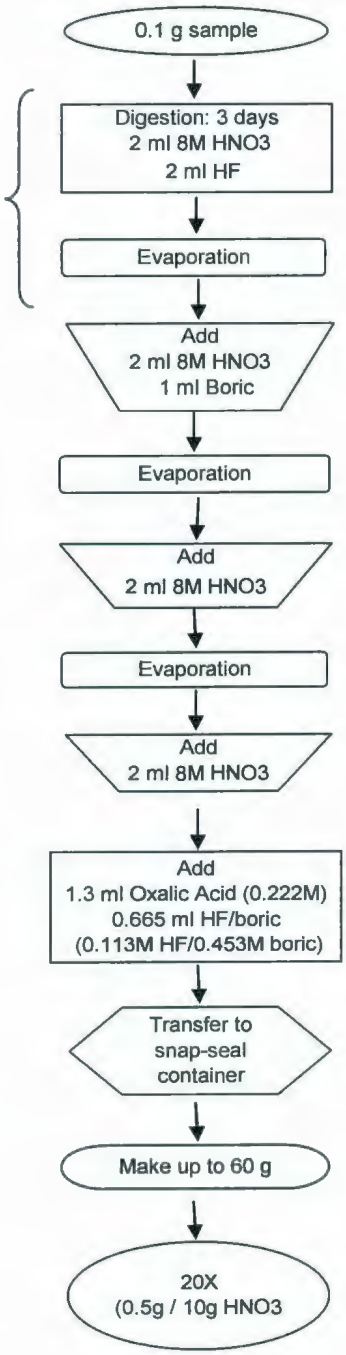
T: 70°C aprox.

2 Cycles



Appendix 20. Trial 10 (T 10) -2 mL HF, heating $H_2C_2O_4$, 8:1 HF/ H_3BO_3.

T: 70°C aprox.



Appendix 21. Second set of experiments (CV-2, CV1, NIST 688-T0, NIST 688-T9, NIST 688-T10).

Element	D.L.	CV-2			CV-1	NIST 688-T0			NIST 688-T9			NIST 688-T10		
Li	8.1	5.7	6.8	42.2	6.6	9.8	9.7	9.3	10.4	10.0	13.9	10.0	9.0	10.9
Ti	2.65	52	52	58	63	6652	6575	5983	6074	6783	6545	6477	6405	6284
V	0.34	6.97	7.64	8.04	7.06	240	238	225	226	245	229	227	234	234
Cr	20	1772	2120	2093	1993	1308	1271	1226	1256	1456	1403	1383	1356	1424
Rb	1.42	<L.D.*	<L.D.*	<L.D.*	<L.D.*	2.05	1.50	2.58	1.52	2.77	1.93	2.47	1.57	1.69
Sr	1.5	4.0	4.8	5.1	5.0	151	150	141	142	152	144	148	151	144
Y	0.2	3.7	3.8	4.0	3.9	17	16	16	16	17	16	16	17	16
Zr	0.39	5.43	6.05	5.85	4.31	52	52	48	50	52	49	48	51	49
Nb	0.32	1.52	1.60	1.68	1.43	5	5	5	5	5	5	5	5	5
Mo	1.62	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Cs	0.19	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Ba	1.35	6.93	8.26	8.03	8.44	153	151	154	150	152	152	147	162	155
La	0.10	1.89	1.77	1.70	1.87	5	5	5	5	5	5	5	5	5
Ce	0.06	3.73	3.71	3.43	3.73	11	11	11	11	10	10	11	11	11
Pr	0.11	0.43	0.37	0.43	0.39	1.78	1.69	1.69	1.66	1.69	1.66	1.68	1.82	1.70
Nd	0.66	1.12	1.27	1.43	1.41	7.77	7.49	7.41	7.43	7.75	7.61	7.53	7.92	7.37
Sm	0.42	<L.D.*	<L.D.*	0.32	0.31	2.31	2.09	2.14	2.14	2.12	2.12	2.22	2.33	2.33
Eu	0.12	<L.D.*	<L.D.*	0.12	<L.D.*	0.95	0.86	0.89	0.88	0.93	0.88	0.91	1.01	0.90
Gd	0.35	<L.D.*	<L.D.*	<L.D.*	<L.D.*	2.03	2.00	1.93	2.05	2.02	1.96	2.01	2.08	2.01
Tb	0.06	<L.D.*	<L.D.*	<L.D.*	<L.D.*	0.43	0.39	0.41	0.39	0.40	0.39	0.45	0.40	0.41
Dy	0.26	0.43	0.49	0.50	0.47	3.24	3.19	3.18	3.10	3.01	3.11	3.07	3.24	3.13
Ho	0.04	0.09	0.09	0.12	0.10	0.69	0.68	0.67	0.66	0.67	0.65	0.67	0.68	0.67
Er	0.22	0.26	0.31	0.40	0.32	2.01	1.94	1.93	1.89	1.86	1.92	1.96	2.05	1.95
Tm	0.06	0.06	<L.D.*	0.10	<L.D.*	0.33	0.30	0.29	0.31	0.29	0.31	0.30	0.33	0.34
Yb	0.31	<L.D.*	<L.D.*	<L.D.*	<L.D.*	1.93	1.90	1.82	1.80	1.87	1.95	1.90	1.89	1.90
Lu	0.07	<L.D.*	<L.D.*	<L.D.*	<L.D.*	0.30	0.29	0.28	0.27	0.29	0.30	0.29	0.30	0.30
Hf	0.36	<L.D.*	<L.D.*	<L.D.*	<L.D.*	1.45	1.42	1.35	1.37	1.41	1.47	1.48	1.46	1.36
Ta	0.07	9.03	9.88	9.61	8.52	0.25	0.22	0.21	0.22	0.22	0.26	0.23	0.25	0.26
Tl	0.10	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Pb	2.03	<L.D.*	<L.D.*	<L.D.*	<L.D.*	3.60	2.36	2.23	2.17	2.68	4.06	2.37	2.62	2.97
Bi	0.11	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Th	0.05	0.08	0.10	0.08	<L.D.*	0.37	0.31	0.34	0.35	0.33	0.33	0.34	0.36	0.32
U	0.06	<L.D.*	<L.D.*	0.07	<L.D.*	0.25	0.31	0.25	0.23	0.48	0.25	0.26	0.28	0.24

*Values below the limit of detection of the instrument.

Appendix 22. Second set of experiments (MESS-T0, MESS-T1, MESS-T2, CV-0-A-T0, and CV-0-A-T9).

Sample	LD	MESS-T0			MESS-T1			MESS-T2			CV-0-A-T0			CV-0-A-T9	
Li	2.83	67	68	59	63	64	65	66	66	65	33	13	4.7	1.4	4.8
Ti	2.80	3597	3393	3617	3835	3874	3810	3888	3878	3598	53	69	44	43	49
V	0.26	206	194	197	213	210	211	215	215	202	7.2	7.7	6.8	6.7	7.0
Cr	4.58	596	515	530	576	606	552	622	584	533	1610	1855	1384	1237	1258
Rb	2.16	114	114	115	128	121	114	103	123	130	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Sr	1.98	110	111	107	120	111	110	105	113	115	4.7	5.3	4.83	6.9	4.97
Y	0.18	19	19	18	20	20	20	20	22	21	3.7	3.8	3.7	4.0	4.0
Zr	0.43	106	104	104	106	113	108	109	115	104	4.9	4.6	4.4	5.1	5.0
Nb	0.27	17	17	17	18	17	17	17	18	17	1.4	1.7	1.5	1.7	1.6
Mo	1.60	2.9	3.0	2.8	2.7	3.2	3.1	2.9	3.0	2.9	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Cs	0.67	8.2	8.0	7.8	8.2	8.4	8.3	8.2	8.5	8.5	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Ba	0.88	1137	1092	1104	1151	1144	1143	1134	1181	1138	7.2	8.3	7.5	7.0	6.9
La	0.11	34	34	33	36	33	35	34	37	37	2.2	1.9	2.6	2.1	2.8
Ce	0.10	57	61	56	63	59	62	62	67	66	4.1	3.7	4.1	4.1	5.0
Pr	0.09	7.7	7.8	7.5	8.2	7.5	8.0	7.8	8.5	8.4	0.5	0.5	0.5	0.5	0.5
Nd	0.96	26	28	26	28	26	27	28	29	29	1.45	1.59	1.71	1.80	1.66
Sm	0.47	5.0	5.1	4.9	5.3	5.0	5.1	5.2	5.7	5.7	<L.D.*	<L.D.*	0.55	<L.D.*	<L.D.*
Eu	0.13	1.04	1.02	1.01	1.09	1.07	1.08	1.11	1.18	1.12	<L.D.*	0.13	0.16	0.19	0.17
Gd	0.25	1.80	1.68	1.64	1.68	1.76	1.53	1.73	1.76	1.88	0.27	0.31	0.34	0.46	0.38
Tb	0.07	0.36	0.36	0.35	0.38	0.33	0.38	0.40	0.40	0.39	<L.D.*	<L.D.*	0.07	0.08	<L.D.*
Dy	0.19	3.48	3.40	3.33	3.67	3.65	3.67	3.93	4.07	3.84	0.52	0.49	0.59	0.63	0.55
Ho	0.05	0.68	0.69	0.68	0.73	0.71	0.70	0.75	0.80	0.76	0.11	0.10	0.12	0.13	0.11
Er	0.22	13	15	14	2.05	2.03	2.07	2.18	2.26	2.15	0.35	0.33	0.38	0.43	0.37
Tm	0.05	0.31	0.31	0.28	0.35	0.32	0.33	0.35	0.38	0.36	0.07	0.07	0.09	0.08	0.08
Yb	0.39	1.90	1.72	1.79	1.88	1.83	1.92	2.04	2.11	1.96	<L.D.*	<L.D.*	<L.D.*	0.39	<L.D.*
Lu	0.06	0.29	0.28	0.29	0.30	0.30	0.31	0.33	0.32	0.32	<L.D.*	<L.D.*	<L.D.*	0.07	0.06
Hf	0.31	3.03	2.69	2.98	2.91	3.14	2.94	3.02	3.15	2.95	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Ta	0.07	0.88	0.83	0.85	0.87	0.88	0.89	0.87	0.88	0.87	6.98	7.65	6.51	6.82	5.50
Tl	0.11	0.95	0.89	0.89	1.03	1.03	0.98	0.92	0.97	0.94	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Pb	2.02	19	20	19	20	20	20	16	19	19	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Bi	0.11	0.34	0.27	0.27	0.31	0.34	0.29	0.24	0.35	0.46	<L.D.*	<L.D.*	<L.D.*	0.12	<L.D.*
Th	0.05	10.2	10.8	10.5	11.9	10.7	11.2	10.9	12.1	11.8	<L.D.*	<L.D.*	0.11	0.12	0.10
U	0.06	2.87	3.05	2.91	3.20	3.07	3.02	3.18	3.45	3.31	<L.D.*	<L.D.*	0.07	<L.D.*	0.06

*Values below the limit of detection of the instrument.

Appendix 23. Second set of experiments (AVG-T0, AVG-T9, AVG-T10, SY-T0, SY-T9, SY-T10).

Sample	LD	AVG-T0			AVG-T9			AVG-T10			SY-T0			SY-T9			SY-T10		
Li	4.44	25.0	20.8	19.0	19.4	18.9	17.4	16.1	16.5	17.7	91.7	101	94.6	91.1	96.2	91.4	87.9	83.9	<L.D.*
Ti	5.10	7736	6491	6473	7110	6312	5946	6016	6111	6539	815	914	876	868	814	774	779	766	788
V	0.34	151	126	128	138	122	113	115	119	127	51	57	54	53	49	47	48	47	49
Cr	8.48	534	462	432	546	447	436	408	435	482	381	429	392	383	343	321	318	321	335
Rb	2.18	79.8	63.2	41.5	62.4	60.0	58.3	62.5	60.4	63.1	195	224	208	207	209	202	203	194	201
Sr	3.63	744	545	553	590	575	565	587	580	602	236	267	252	252	257	246	251	237	245
Y	0.36	22.3	18.2	18.1	18.9	18.3	17.1	17.8	17.4	17.8	104	119	112	112	114	111	112	106	109
Zr	0.96	258	211	215	219	217	199	206	204	208	249	280	273	275	273	266	274	251	267
Nb	0.55	20.5	16.4	16.6	16.9	16.5	15.3	15.7	15.4	15.7	31.7	36.4	34.7	34.9	34.6	34.0	34.0	32.1	33.4
Mo	3.09	6.83	5.04	4.43	4.16	3.50	2.95	3.16	2.44	2.55	2.50	2.55	2.63	2.12	2.10	1.69	2.14	1.53	2.15
Cs	0.40	2.61	2.13	1.87	1.96	1.84	1.71	1.73	1.68	1.70	2.65	2.98	2.75	2.85	2.84	2.66	2.72	2.50	2.64
Ba	3.41	1849	1483	1449	1531	1502	1419	1415	1424	1464	381	435	420	403	420	401	402	381	405
La	0.26	46.1	34.1	31.4	36.7	35.4	35.2	35.5	35.9	36.6	63.7	71.7	68.8	67.7	69.9	65.3	66.1	64.0	65.6
Ce	0.29	77.0	60.0	57.1	63.1	61.4	59.9	59.2	60.5	61.9	138	156	149	145	156	145	145	139	146
Pr	0.25	10.37	7.55	7.20	8.21	7.85	7.79	7.85	7.93	8.02	18.5	20.7	19.6	19.3	19.9	18.9	19.0	18.4	19.1
Nd	2.58	39.3	28.7	27.5	29.5	28.6	27.8	28.3	28.5	28.6	67.0	76.9	72.6	71.6	75.1	69.7	70.4	67.2	69.9
Sm	1.53	8.49	6.07	5.79	5.84	5.81	5.34	5.52	5.29	5.20	15.5	17.0	15.8	15.5	16.0	14.8	15.5	14.7	15.3
Eu	0.45	2.44	1.83	1.71	1.81	1.63	1.52	1.58	1.52	1.47	2.52	2.86	2.70	2.58	2.66	2.47	2.52	2.29	2.50
Gd	0.85	2.97	2.25	2.11	1.92	1.98	1.58	1.97	1.86	1.74	9.39	11.4	10.4	10.1	10.0	9.63	10.1	9.41	9.89
Tb	0.20	0.62	0.48	0.41	0.43	0.39	0.38	0.36	0.33	0.34	2.14	2.44	2.26	2.23	2.36	2.18	2.25	2.10	2.14
Dy	0.70	4.99	3.81	3.61	3.66	3.46	3.23	3.31	3.23	3.16	18.0	20.6	19.0	19.0	19.6	18.3	18.9	17.8	18.6
Ho	0.19	1.00	0.74	0.69	0.69	0.67	0.59	0.61	0.58	0.56	4.11	4.70	4.41	4.42	4.49	4.19	4.33	4.07	4.25
Er	0.78	3.35	2.20	2.06	1.98	1.87	1.65	1.72	1.55	1.54	13.4	15.3	14.2	14.3	14.7	13.7	14.0	13.3	13.8
Tm	0.19	0.53	0.40	0.33	0.34	0.28	0.28	0.26	0.24	0.24	2.26	2.59	2.37	2.42	2.37	2.32	2.30	2.26	2.28
Yb	0.97	2.97	2.23	2.16	1.89	1.69	1.49	1.39	1.32	1.31	15.9	17.8	16.7	16.5	17.2	16.1	16.8	15.7	16.1
Lu	0.20	0.53	0.38	0.34	0.30	0.27	0.23	0.25	0.18	0.17	2.68	3.00	2.92	2.85	2.80	2.67	2.75	2.61	2.73
Hf	1.04	7.45	5.80	5.37	5.31	5.27	4.81	4.82	4.67	4.57	7.89	8.72	8.56	8.40	7.90	7.89	8.35	7.55	7.74
Ta	0.19	1.27	0.98	0.86	0.87	0.84	0.72	0.75	0.72	0.73	1.68	1.91	1.83	1.81	1.78	1.68	1.74	1.68	1.68
Tl	0.32	1.03	0.79	0.63	0.71	0.58	0.55	0.54	0.44	0.49	2.63	2.93	2.75	2.62	2.64	2.51	2.48	2.38	2.46
Pb	0.83	42.4	34.7	32.1	33.6	32.8	32.0	33.9	31.4	31.9	80.2	89.8	85.2	84.4	86.1	81.4	83.0	79.5	81.3
Bi	0.31	0.46	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*
Th	0.26	7.94	5.87	5.75	6.03	6.07	5.97	5.83	5.89	5.91	345	385	361	359	359	349	359	343	358
U	0.19	2.45	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	<L.D.*	230	256	271	258	255	243	248	218	245

*Values below the limit of detection of the instrument.

Appendix 24. Third set of experiments.

		CV-0-A									CV-0-B									CV-1								
Element	LD	T0			T9			T10			T0			T9			T10			T0			T9			T10		
Li	0.75	1.13	1.09	1.33	1.21	1.12	1.03	0.99	1.27	1.15	2.29	1.13	0.93	0.89	1.14	1.03	1.01	3.07	1.14	1.13	1.29	1.33	1.12	1.29	1.18	1.60	1.31	1.33
Ti	3.16	44.5	49.6	53.2	45.3	54.3	40.4	51.3	47.4	51.0	75.8	72.9	72.9	78.2	72.9	73.8	69.5	71.9	68.3	205	193	199	185	194	202	197	190	174
V	0.16	7.15	6.78	6.58	6.8	6.60	6.06	7.86	7.93	8.21	10.4	10.8	10.3	10.3	10.3	10.3	9.03	9.90	9.27	18.8	18.9	19.5	17.7	18.6	18.5	18.5	18.5	17.2
Cr	1.80	69.4	61.4	55.9	57.8	54.2	51.5	64.1	63.0	63.5	329	337	339	333	336	327	274	282	275	439	438	451	441	439	432	436	434	425
Rb	0.34	1.19	0.55	0.89	1.21	0.57	0.42	0.90	0.70	0.41	1.07	0.69	0.45	0.89	0.72	0.56	1.32	0.65	<0.34	1.35	1.00	0.84	1.57	1.08	0.79	1.92	0.99	1.04
Sr	2.28	6.98	6.88	11.9	6.84	6.32	7.35	6.51	6.79	6.31	8.97	9.46	21.15	8.79	8.82	9.15	8.41	8.94	9.02	13.3	15.1	14.7	13.9	14.8	14.2	14.1	14.0	14.1
Y	0.14	4.30	4.00	3.90	4.12	3.78	4.27	4.37	4.38	4.27	3.87	3.98	4.16	3.85	3.68	3.91	3.47	3.70	3.47	6.48	6.56	6.88	6.37	6.53	6.23	6.45	6.49	6.38
Zr	0.33	4.08	4.21	4.36	4.65	4.22	4.64	7.18	5.71	5.40	5.53	5.42	5.03	5.48	5.50	6.50	8.00	4.82	5.50	6.52	6.75	8.73	6.65	6.32	6.84	6.84	6.85	6.29
Nb	0.19	1.74	1.62	1.62	1.656	1.57	2.19	1.77	1.87	1.69	2.27	2.26	2.10	2.09	2.22	2.18	2.02	2.10	2.08	2.86	2.79	2.99	2.55	2.78	2.78	2.75	2.76	2.58
Mo	1.09	2.27	1.06	2.30	2.557	6.251	1.128	1.43	<1.087	2.917	4.36	3.45	3.22	4.65	4.80	4.99	3.91	3.51	4.98	3.93	4.82	6.28	4.30	4.74	6.72	4.22	4.47	4.69
Cs	0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11	<0.11
Ba	1.46	8.61	8.09	18.15	8.55	8.94	9.23	8.52	9.95	8.71	15.0	13.3	14.0	11.5	13.9	12.2	12.8	11.9	11.0	17.8	18.6	19.0	18.3	19.2	18.2	18.2	19.3	20.1
La	0.10	1.90	1.85	3.09	1.94	1.76	1.94	2.63	1.86	1.90	2.01	2.08	2.43	1.95	2.24	2.04	1.86	1.84	1.88	3.92	3.86	3.95	3.89	4.01	3.88	4.19	4.36	3.92
Ce	0.11	4.15	4.01	5.88	4.19	3.93	4.15	5.01	4.08	4.03	3.59	3.55	4.09	3.41	3.70	3.47	3.24	3.07	3.11	6.79	6.71	6.64	6.73	6.81	6.63	7.46	7.38	6.81
Pr	0.07	0.45	0.46	0.70	0.43	0.44	0.47	0.53	0.46	0.46	0.45	0.51	0.59	0.45	0.53	0.50	0.42	0.46	0.47	0.84	0.87	0.87	0.81	0.90	0.88	0.86	0.90	0.85
Nd	0.69	2.04	1.89	2.96	1.88	1.79	1.84	2.22	1.86	1.76	2.02	2.12	2.23	1.78	2.08	2.06	1.84	2.13	2.08	3.27	3.63	3.43	3.26	3.52	3.34	3.44	3.49	3.38
Sm	0.32	0.52	0.50	0.73	0.51	0.47	0.47	0.50	0.51	0.43	0.47	0.41	0.46	0.35	0.47	0.54	<0.32	0.60	0.55	0.63	0.76	0.79	0.58	0.82	0.66	0.61	0.75	0.64
Eu	0.11	0.21	0.19	0.22	0.19	0.17	0.17	0.19	0.17	0.16	0.17	0.16	0.17	0.16	0.17	0.17	0.17	0.19	0.18	0.25	0.27	0.29	0.25	0.28	0.26	0.24	0.25	0.25
Gd	0.23	0.58	0.54	0.60	0.55	0.50	0.50	0.59	0.56	0.50	0.51	0.51	0.54	0.65	0.52	0.51	0.53	0.54	0.50	0.79	0.84	0.80	0.78	0.90	0.87	0.79	0.82	0.82
Tb	0.05	0.10	0.09	0.10	0.09	0.08	0.08	0.09	0.09	0.08	0.08	0.08	0.09	0.08	0.09	0.08	<0.05	<0.05	<0.05	0.12	0.13	0.14	0.11	0.12	0.12	0.12	0.12	0.12
Dy	0.18	0.69	0.59	0.62	0.61	0.58	0.64	0.67	0.64	0.59	0.57	0.58	0.61	0.54	0.56	0.55	0.54	0.55	0.53	0.88	0.95	0.97	0.86	0.94	0.92	0.87	0.90	0.89
Ho	0.04	0.14	0.14	0.14	0.15	0.13	0.14	0.15	0.15	0.14	0.12	0.13	0.13	0.12	0.12	0.12	0.11	0.12	0.12	0.20	0.21	0.21	0.20	0.20	0.20	0.20	0.19	0.19
Er	0.16	0.50	0.48	0.49	0.47	0.50	0.48	0.46	0.48	0.40	0.40	0.37	0.46	0.37	0.40	0.41	0.37	0.39	0.42	0.58	0.71	0.68	0.59	0.64	0.62	0.61	0.63	0.65
Tm	0.04	0.08	0.10	0.10	0.07	0.10	0.11	0.06	0.11	0.10	0.06	0.09	0.10	0.05	0.09	0.09	<0.04	<0.04	<0.04	0.08	0.13	0.13	0.08	0.13	0.12	0.09	0.11	0.11
Yb	0.19	0.53	0.47	0.51	0.46	0.44	0.49	0.46	0.44	0.45	0.38	0.38	0.43	0.36	0.41	0.38	0.38	0.44	0.41	0.61	0.63	0.66	0.54	0.64	0.62	0.55	0.65	0.60
Lu	0.04	0.07	0.07	0.07	0.07	0.06	0.07	0.06	0.06	0.06	0.06	0.05	0.06	0.05	0.05	0.05	0.05	0.06	0.05	0.08	0.09	0.08	0.07	0.08	0.08	0.08	0.09	0.08
Hf	0.20	<0.195	<0.195	<0.195	<0.195	<0.195	<0.195	<0.105	<0.105	<0.105	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Ta	0.04	1.61	1.62	1.56	1.537	1.465	1.549	1.53	1.58	1.50	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Tl	0.20	<0.198	<0.198	<0.198	<0.198	<0.198	<0.198	<0.198	<0.198	<0.198	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Pb	0.46	0.53	0.45	1.61	0.547	1.781	<0.459	0.68	<0.459	1.923	0.72	0.69	0.54	0.46	0.52	0.54	<0.46	<0.46	<0.46	<0.46	0.54	0.70	0.52	0.51	0.46	1.06	0.51	0.59
Bi	0.07	<0.067	<0.067	<0.067	0.136	<0.067	0.07	0.32	0.1	0.0	0.11	0.11	0.09	<0.07	0.18	0.12	<0.07	<0.07	<0.07	<0.07	<0.07	<0.07	0.13	<0.07	0.08	<0.07	<0.07	<0.07
Th	0.05	0.09	0.10	0.12	0.121	0.076	0.064	0.09	0.1	0.1	0.08	0.07	0.11	0.09	0.08	0.08	0.10	0.10	0.09	0.21	0.20	0.21	0.21	0.22	0.21	0.23	0.23	0.21
U	0.05	0.07	0.09	0.11	0.07	0.09	0.083	0.06	0.1	0.1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.08	0.07	<0.05	0.08	0.06	<0.05	0.06	0.06

***Values below the limit of detection of the instrument.**

Appendix 24. (Continued).

Element	LD	CV-5									CV-10								
		T0			T9			T10			T0			T9			T10		
Li	0.22	1.09	0.81	0.71	0.91	0.58	0.72	0.82	0.97	0.49	0.80	1.23	1.02	0.81	1.17	1.59	1.27	1.51	1.04
Ti	4.05	205	197	183	167	219	224	219	196	182	112.6	131.2	137.9	112	125	133	149	152	155
V	0.27	16.8	17.9	14.8	16.0	17.5	17.4	18	18	16	10.5	12.6	13.6	10.6	11.3	11.6	15.1	15.9	14.9
Cr	2.12	279	288	269	264	280	281	289	289	250	231	260	309	218	209	209	332	340	266
Rb	0.69	1.52	0.95	0.70	1.36	1.05	<LD.*	1.92	1.21	0.71	1.42	1.12	0.92	1.49	1.06	1.08	1.68	1.14	0.87
Sr	2.62	12.6	12.3	11.8	11.2	11.2	11.4	12.5	11.6	10.5	10.6	11.2	11.5	9.95	11.3	13.5	11.3	11.2	10.2
Y	0.26	6.55	6.34	6.14	5.99	5.98	6.34	6.64	5.88	5.46	5.44	5.48	5.40	5.03	5.46	5.75	5.94	5.68	5.54
Zr	0.48	5.33	5.15	4.18	4.56	4.80	3.98	6.35	5.47	3.90	3.76	5.43	4.42	3.91	4.23	7.91	4.14	4.75	5.80
Nb	0.35	1.88	1.78	1.49	1.65	1.75	1.77	2.00	1.95	1.72	1.36	1.51	1.56	1.26	1.44	1.47	1.51	1.55	1.55
Mo	2.06	4.24	4.17	4.89	3.55	2.85	2.87	3.12	2.75	2.56	2.31	2.63	2.56	2.58	2.30	2.88	2.46	3.09	2.69
Cs	0.18	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*
Ba	1.87	17.6	24.4	17.9	16.7	16.8	17.6	17.9	17.3	14.8	16.1	17.1	17.7	17.72	25.05	18.58	17.5	18.5	16.8
La	0.15	3.28	3.13	3.56	3.26	3.08	3.47	3.38	3.34	2.85	2.63	2.73	2.92	2.74	2.78	4.03	2.88	2.74	3.00
Ce	0.15	5.32	5.06	5.63	5.12	5.04	5.47	5.50	5.26	4.45	4.87	4.91	5.19	4.86	4.78	5.86	5.15	4.86	5.21
Pr	0.12	0.73	0.75	0.79	0.69	0.70	0.78	0.71	0.78	0.63	0.60	0.65	0.68	0.60	0.63	1.16	0.64	0.65	0.66
Nd	0.84	3.34	3.18	3.11	2.92	2.67	3.07	3.16	3.01	2.37	2.57	2.57	2.64	2.48	2.56	3.44	2.77	2.40	2.55
Sm	0.47	0.81	0.66	0.61	0.59	0.54	0.60	0.69	0.58	0.49	0.55	0.56	0.51	0.51	0.56	0.92	0.56	0.52	0.47
Eu	0.15	0.29	0.23	0.22	0.24	0.20	0.23	0.27	0.22	0.19	0.22	0.20	0.19	0.21	0.20	0.19	0.21	0.20	0.18
Gd	0.32	0.81	0.75	0.73	0.81	0.74	0.76	0.86	0.75	0.66	0.76	0.72	0.69	0.73	0.70	0.67	0.73	0.67	0.64
Tb	0.10	0.17	0.13	0.11	0.12	0.12	0.11	0.13	0.12	0.09	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dy	0.34	0.94	0.83	0.84	0.85	0.79	0.85	0.92	0.85	0.77	0.83	0.78	0.76	0.75	0.74	0.76	0.78	0.74	0.75
Ho	0.11	0.22	0.20	0.19	0.19	0.17	0.19	0.19	0.20	0.16	0.18	0.17	0.16	0.17	0.16	0.17	0.17	0.16	0.16
Er	0.34	0.71	0.63	0.59	0.59	0.60	0.61	0.63	0.61	0.58	0.54	0.54	0.56	0.55	0.54	0.75	0.54	0.54	0.49
Tm	0.10	0.11	0.13	0.12	<0.103	0.11	0.12	0.08	0.13	<0.103	<0.10	0.12	0.11	<0.1	<0.1	0.38	<0.1	<0.1	<0.1
Yb	0.35	0.70	0.61	0.58	0.56	0.56	0.58	0.63	0.53	0.46	0.55	0.53	0.48	0.54	0.53	0.46	0.52	0.50	0.45
Lu	0.05	0.09	0.08	0.08	0.08	0.07	0.07	0.08	0.08	0.06	0.08	0.07	0.07	0.07	0.07	0.06	0.07	0.07	0.06
Hf	0.27	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	0.04	0.05	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*
Ta	0.06	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*
Tl	0.20	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	0.33	<LD.*	<LD.*	<LD.*
Pb	1.44	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*
Bi	0.09	0.17	0.11	0.12	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*
Th	0.07	0.15	0.09	0.09	0.13	0.08	0.11	0.11	0.15	0.08	2.09	0.13	0.08	0.10	<LD.*	<LD.*	0.09	0.07	0.08
U	0.09	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	<LD.*	0.33	<0.09	<0.09	<0.09

*Values below the limit of detection of the instrument.

Appendix 25. Third set of experiments (2 months later).

Element	LD	CV-0-A									CV-0-B								
		T0			T9			T10			T0			T9			T10		
Li	13.4	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Ti	106	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	83.1
V	7.7	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	8.46	8.31	9.06	8.90	10.6	10.5	11.6	12.5	11.2
Cr	8.6	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	318	306	320	265	318	283	291	295	273
Cr	76	344	323	339	379	451	414	451	456	495	859	779	764	589	693	657	677	675	474
Rb	2.1	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Sr	14.1	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Y	1.3	3.14	2.69	2.71	2.60	3.11	3.58	3.14	3.05	3.28	3.27	2.80	2.65	3.11	3.33	3.65	3.92	4.10	3.89
Zr	3.2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	2.79	2.84	3.08	3.83	4.66	4.80	6.48	5.83	5.38
Nb	2.2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.72	0.79	0.63	1.13	1.44	1.59	1.79	1.92	2.29
Mo	12.0	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Cs	1.1	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Ba	11.8	30.64	<DL	13.09	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	12.96	<DL	12.66	<DL	12.62
La	0.9	1.21	1.12	1.42	1.19	1.16	1.39	<DL	<DL	<DL	1.55	1.41	1.56	1.58	2.03	1.87	2.02	1.78	1.98
Ce	0.8	3.24	2.91	3.33	2.86	3.31	3.23	3.96	3.77	3.34	2.92	2.63	2.78	2.92	3.56	3.08	3.41	3.16	3.11
Pr	0.7	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Nd	6.2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Sm	3.2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Eu	1.00	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Gd	1.8	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Tb	0.33	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Dy	1.33	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Ho	0.34	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Er	1.36	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Tm	0.31	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Yb	1.95	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Lu	0.41	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Hf	1.48	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Ta	0.38	2.26	2.12	2.24	1.97	2.36	2.49	2.12	2.04	2.25	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Tl	0.91	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Pb	1.92	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Bi	0.78	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Th	0.56	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
U	0.38	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL

*Values below the limit of detection of the instrument.

Appendix 25. (Continued).

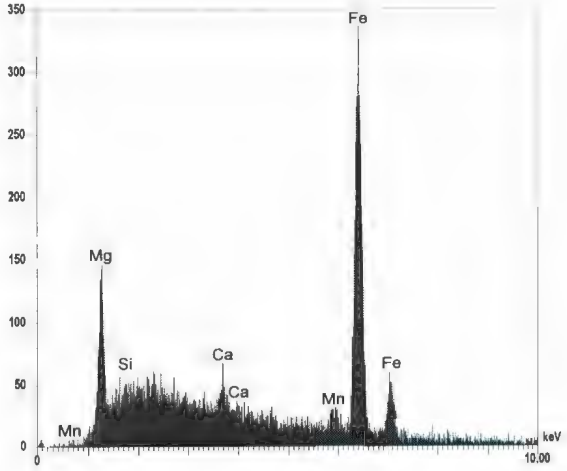
Element	DL	CV-1									CV-5									DL	CV-10								
		T0			T9			T10			T0			T9			T10				T0			T9			T10		
Li	10.9	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	12.9	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Ti	29.7	199	174	164	164	179	177	197	179	173	195	193	195	189	242	228	239	218	192	26.9	128	151	152	153	153	158	173	163	159
V	2.33	18.4	17.3	16.7	15.2	16.8	15.9	18.4	17.0	16.8	16.1	17.3	15.6	17.7	19.2	17.8	20.5	20.7	18.5	1.94	12.6	15.4	16.8	15.1	15.2	15.6	17.7	17.2	16.1
Cr	2	336	319	306	304	323	289	327	302	318	195	186	203	209	207	196	234	252	199	3	223	245	308	249	237	233	327	309	235
Cr	22	667	613	581	558	607	566	638	582	604	511	513	513	570	588	547	758	768	675	24	519	607	686	605	598	604	740	722	637
Rb	2.63	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	2.29	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Sr	14.7	11.3	11.9	12.4	12.7	15.2	16.1	17.6	18.3	17.1	<DL	20.6	18.0	18.1	22.9	22.2	18.2	14.1	13.6	16.3	<DL	18.2	<DL	16.7	<DL	<DL	<DL	<DL	<DL
Y	1.42	6.29	6.00	5.98	5.61	6.13	5.90	6.38	6.17	6.32	5.98	6.79	6.98	6.63	7.62	6.93	7.53	6.65	5.65	1.48	6.33	6.31	6.32	6.90	6.98	6.09	6.05	6.25	6.23
Zr	3.37	6.6	6.01	6.878	5.109	7	5.92	6.53	7.03	6.76	5.42	6.19	6.07	7.04	6.78	6.54	6.05	5.70	4.48	3.4	4.01	6.07	5.59	5.78	4.97	6.80	5.25	4.45	6.11
Nb	2.17	2.414	2.31	2.327	<DL	2.523	2.62	2.91	2.84	2.94	<DL	2.76	2.19	2.32	3.21	3.01	2.53	2.31	1.79	2.1	<DL	<DL	2.141	<DL	<DL	2.2	<DL	<DL	<DL
Mo	12.7	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	15.9	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Cs	1.0	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.88	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Ba	9.34	16.8	16.9	17.1	16.6	19.7	18.1	18.8	17.9	20.4	17.4	21.9	22.3	20.3	24.7	22.2	<DL	<DL	<DL	27.6	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
La	0.72	3.88	3.61	3.59	3.35	3.81	3.56	4.10	4.09	3.85	3.22	3.63	3.95	3.69	4.08	3.94	3.67	3.51	2.92	0.77	2.99	3.29	3.31	3.19	3.08	3.81	3.26	3.09	3.34
Ce	0.75	6.68	6.13	5.93	5.81	6.26	5.92	6.96	6.61	6.18	4.77	5.36	6.16	5.47	6.07	5.67	5.82	5.47	4.34	0.81	5.23	5.41	5.56	5.54	5.12	6.06	5.46	5.15	5.44
Pr	0.61	0.75	0.74	0.76	0.70	0.85	0.83	0.98	1.06	0.95	0.70	1.04	1.07	0.98	1.15	1.15	0.94	0.89	0.74	0.57	0.80	0.84	0.90	0.81	0.72	0.86	0.76	0.72	0.82
Nd	6.15	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	7.11	6.74	5.11	<DL	<DL	6.15	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Sm	3.56	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	2.42	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Eu	0.86	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.79	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Gd	1.73	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	1.54	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Tb	0.35	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.28	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Dy	1.13	<DL	<DL	<DL	<DL	<DL	<DL	1.085	1.349	1.222	<DL	<DL	<DL	<DL	1.72	1.79	<DL	<DL	<DL	1.40	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Ho	0.32	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.36	<DL	<DL	0.38	0.35	0.306	<DL	<DL	0.28	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Er	1.38	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	1.47	1.42	1.17	<DL	<DL	1.06	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Tm	0.34	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.355	<DL	<DL	<DL	0.27	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Yb	2.03	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	1.80	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Lu	0.35	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.29	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Hf	1.80	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	1.49	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Ta	0.31	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.38	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Tl	0.54	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.68	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Pb	1.38	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	2.42	<DL	<DL	<DL	<DL	1.12	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Bi	0.49	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.59	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Th	0.47	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.40	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
U	0.37	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.29	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL

*Values below the limit of detection of the instrument.

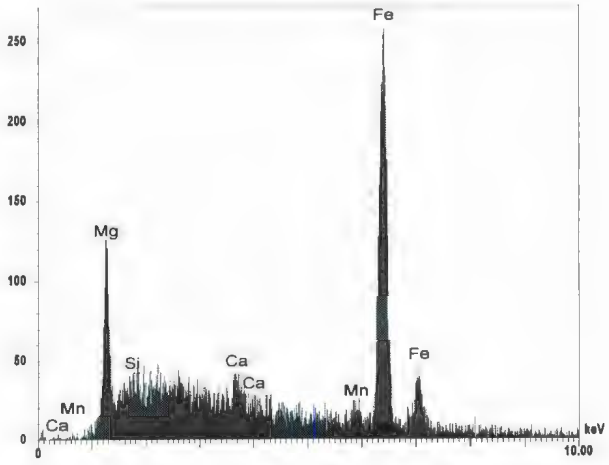
Appendix 26. Energy-dispersive spectra (EDS).

The EDS correspond to the grain number in Identification Key of the SEM Epoxy Mount. (Minerals are abbreviated, See List of abbreviations)

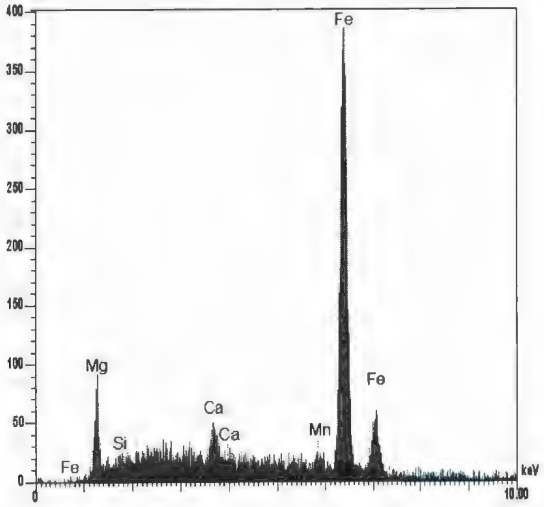
EDS - grain 1: Mg, Ca, Mn, Fe cb



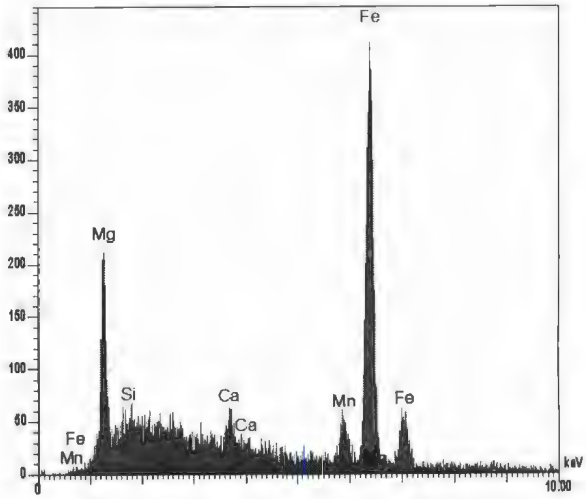
EDS - grain 2: Mg, Ca, Mn, Fe cb



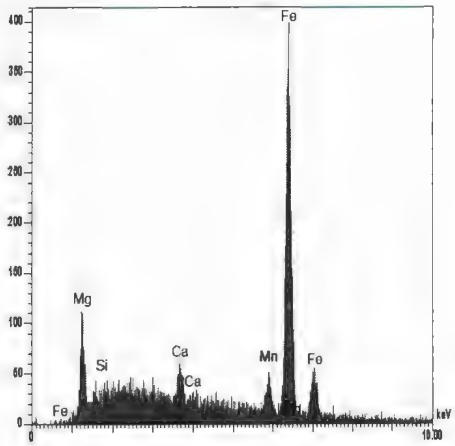
EDS - grain 3: Mg, Ca, Mn, Fe cb



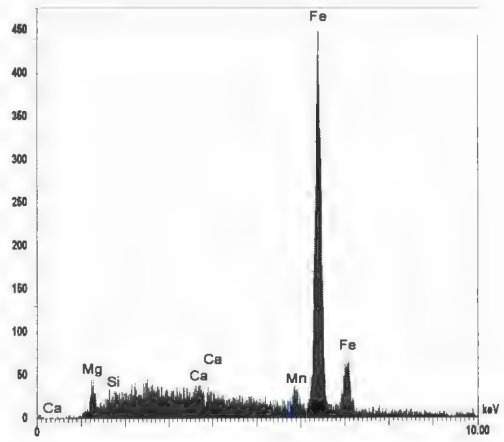
EDS - grain 4: Mg, Ca, Mn, Fe cb



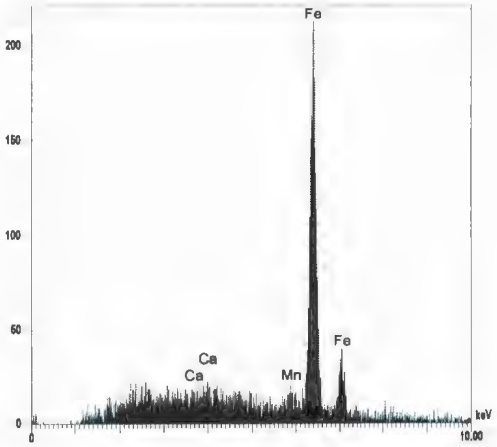
EDS - grain 5: Mg, Ca, Mn, Fe cb



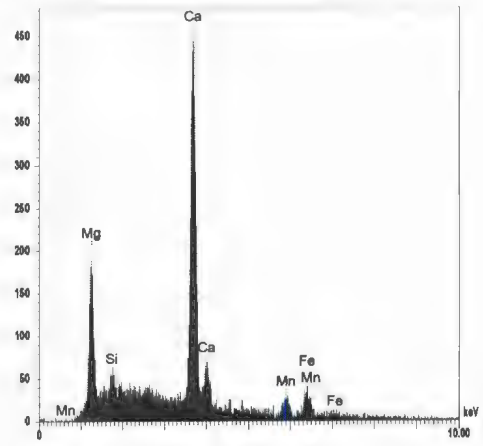
EDS - grain 6: Mg, Ca, Mn, Fe cb



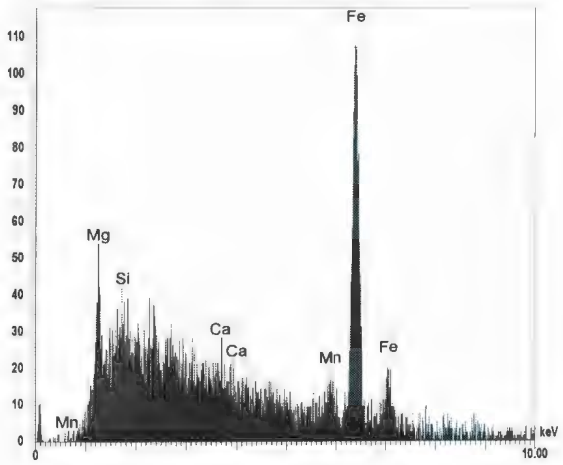
EDS - grain 7: Fe oxide



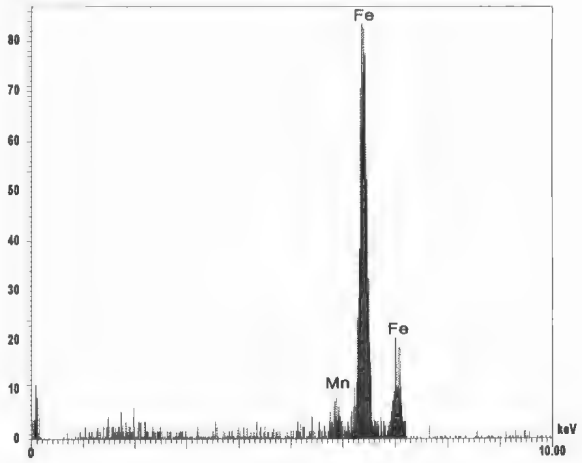
EDS - grain 8: Mg, Ca, Mn, Fe cb



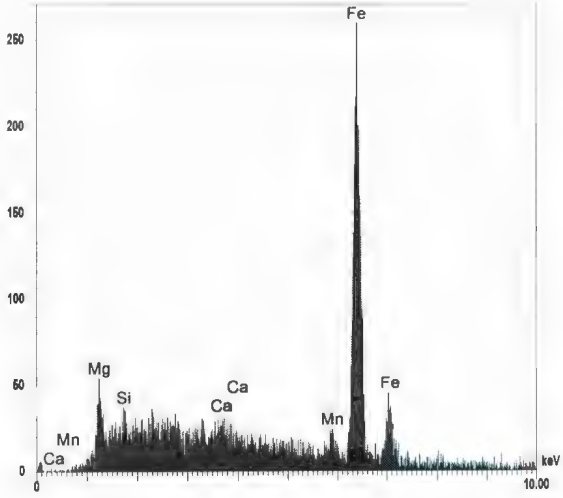
EDS - grain 9: Mg, Ca, Mn, Fe cb



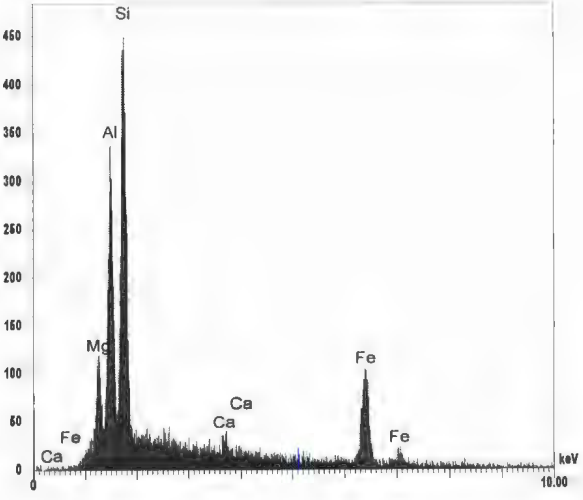
EDS - grain 10: Fe oxide



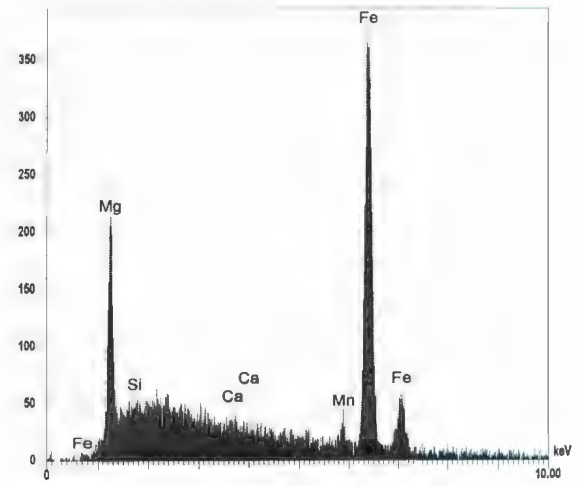
EDS - grain 11: Mg, Ca, Mn, Fe cb



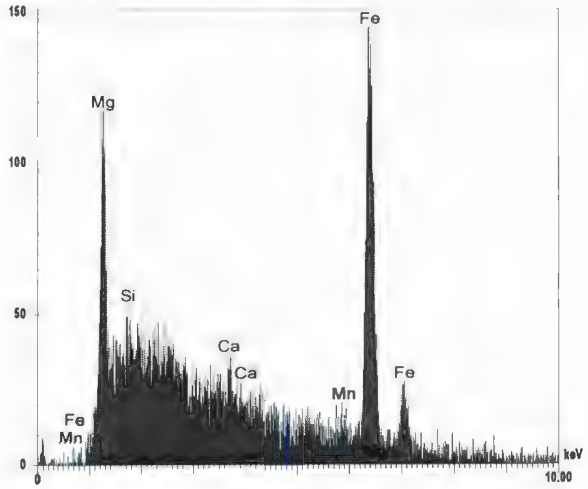
EDS - grain 12: Alm (grt)



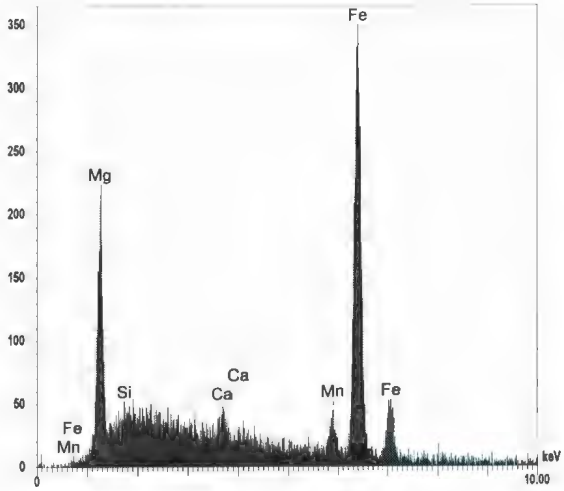
EDS - grain 13: Mg, Ca, Mn, Fe cb



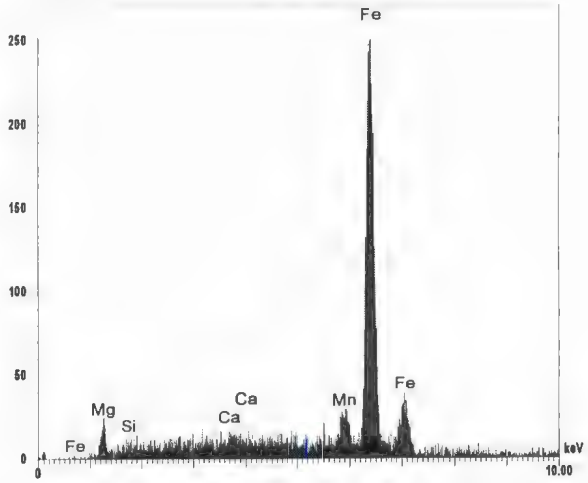
EDS - grain 14: Mg, Ca, Fe, Mn cb



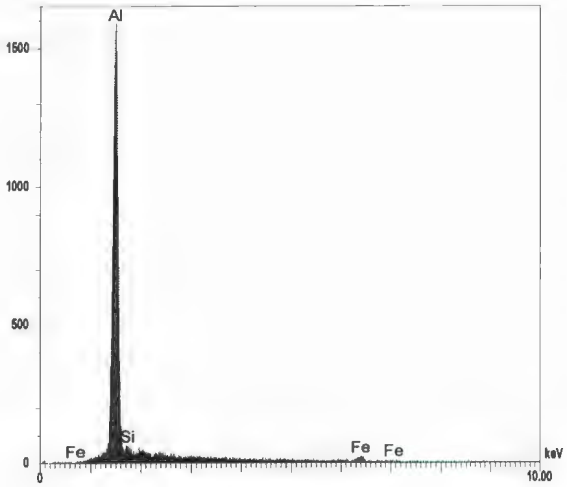
EDS - grain 15: Mg, Ca, Mn, Fe cb



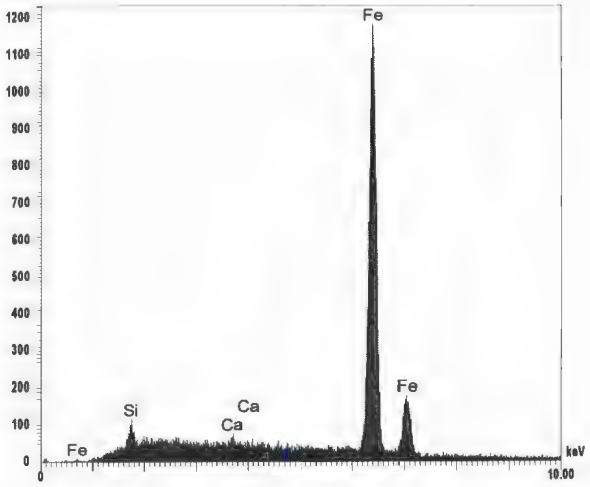
EDS - grain 16: Mg, Ca, Mn, Fe cb



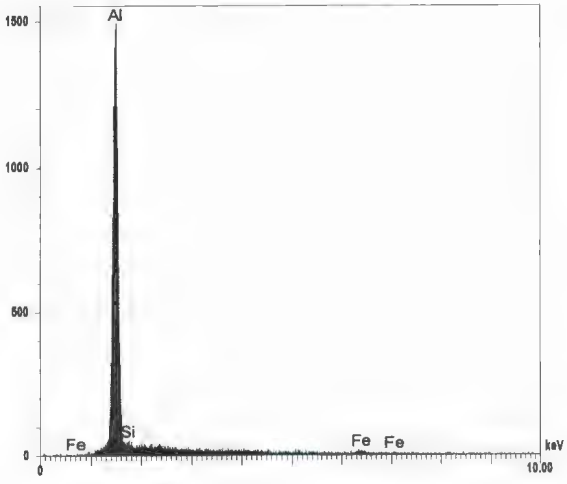
EDS - grain 17: Al oxide



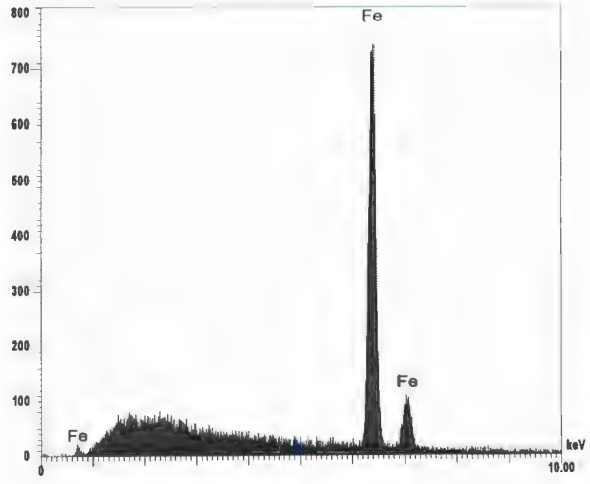
EDS - grain 18: Fe oxide



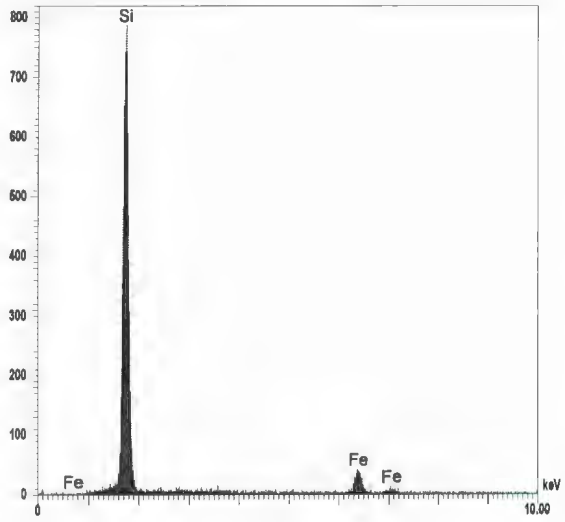
EDS - grain 19: Al oxide



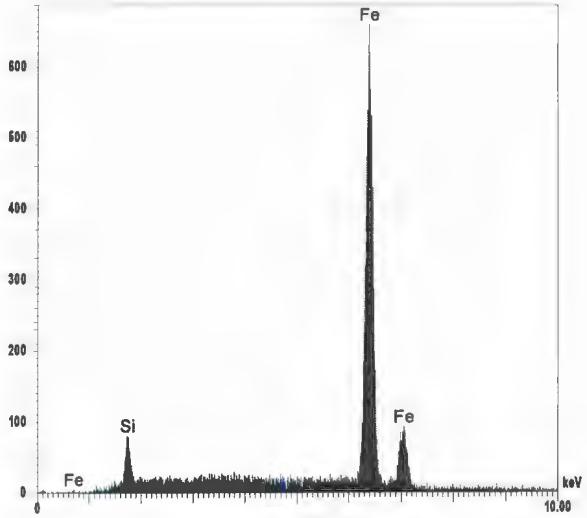
EDS - grain 20: Fe oxide



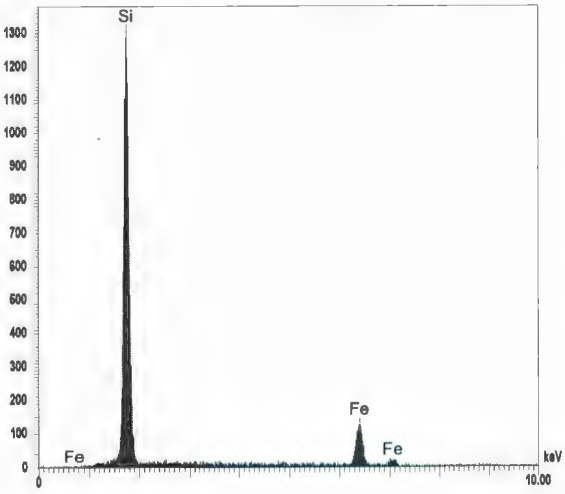
EDS - grain 21: Qtz with Fe oxide inclusion



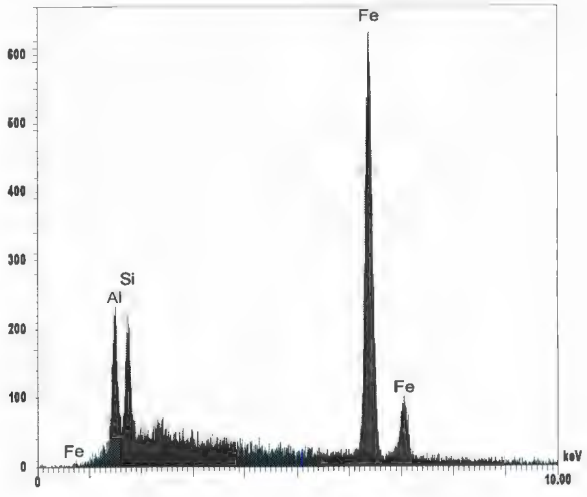
EDS - grain 22: Fe oxide



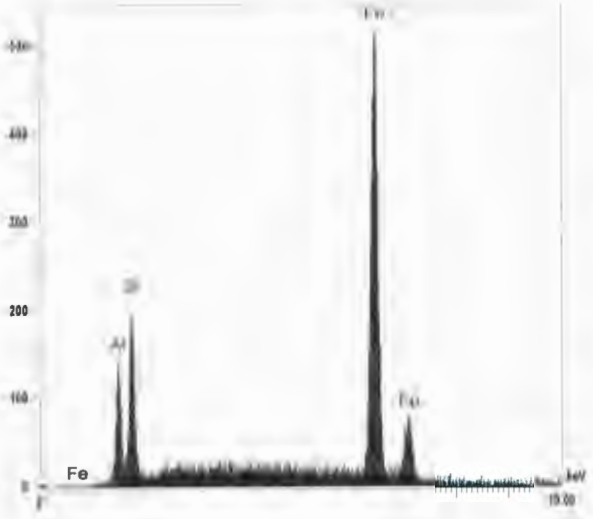
EDS - grain 23: Qtz



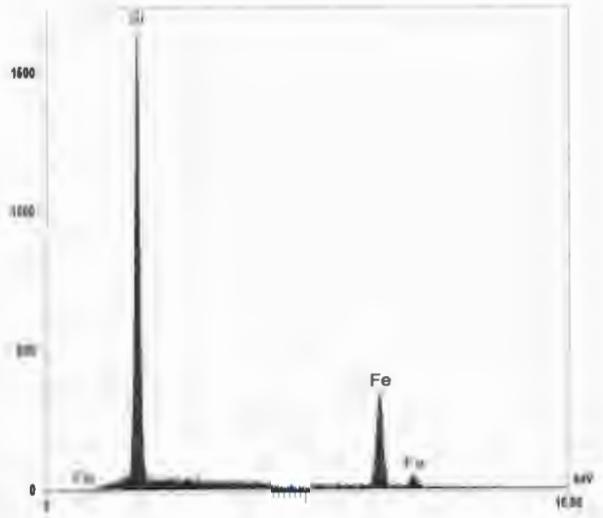
EDS - grain 24: Am (gru)



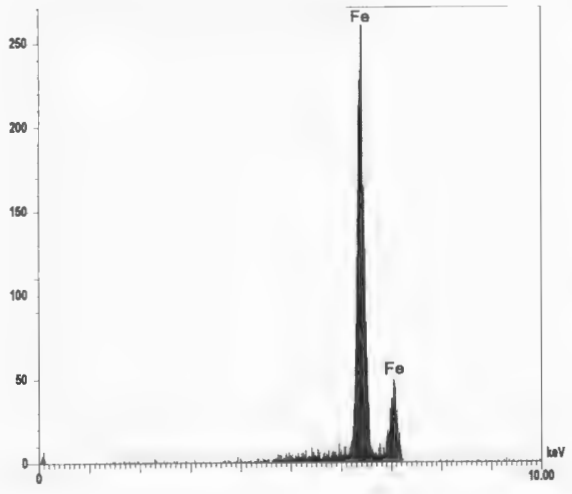
EDS - grain 25: Am (gru)



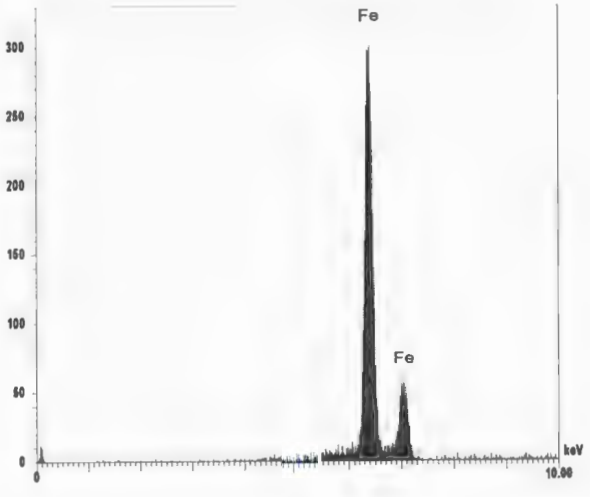
EDS - grain 26: Qtz with Fe oxide inclusion



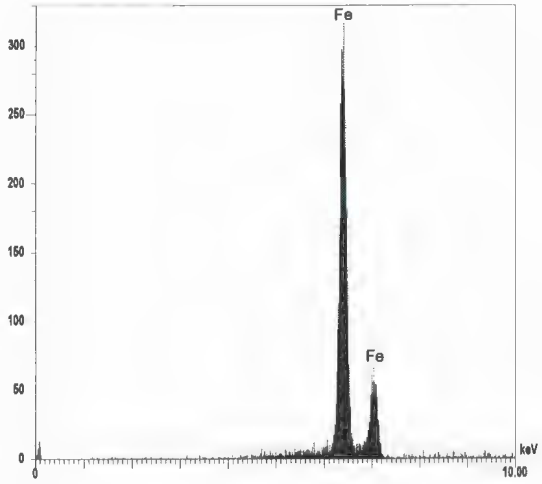
EDS - grain 27: Fe oxide



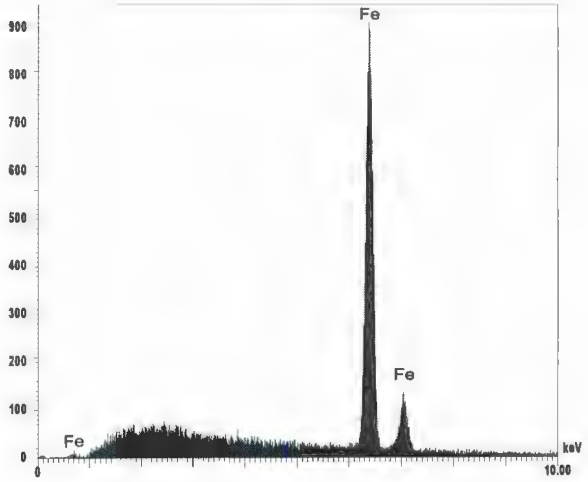
EDS - grain 28: Fe oxide



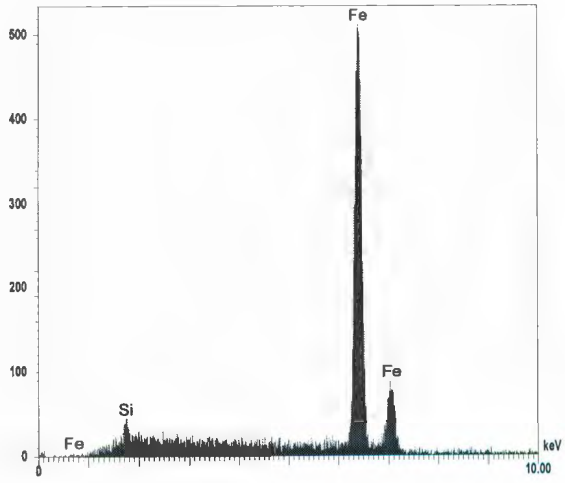
EDS - grain 29: Fe oxide



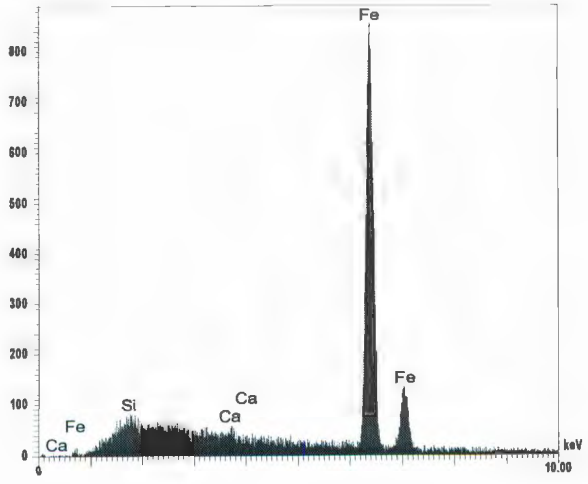
EDS - grain 30: Fe oxide



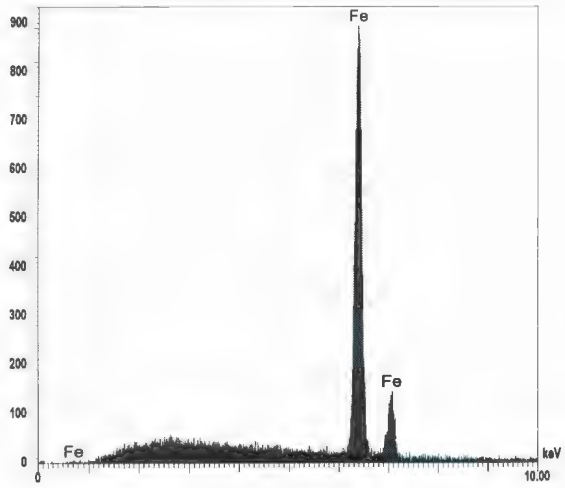
EDS - grain 31: Fe oxide



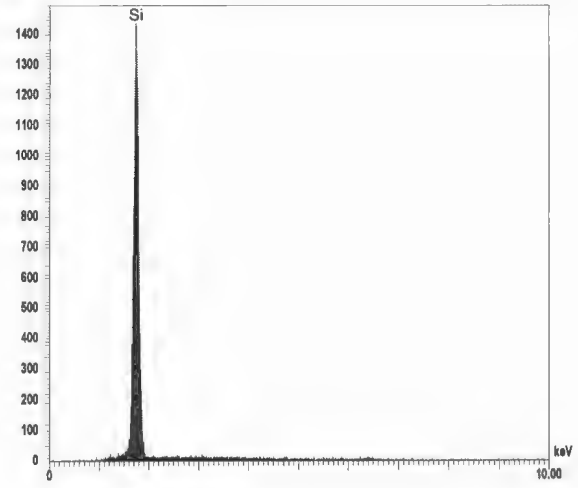
EDS - grain 32: Fe oxide



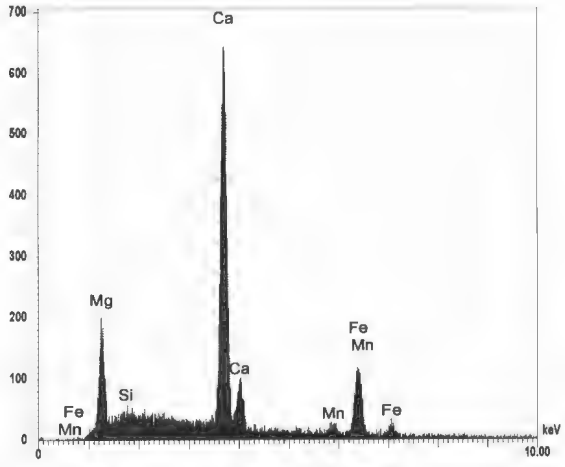
EDS - grain 33: Fe oxide



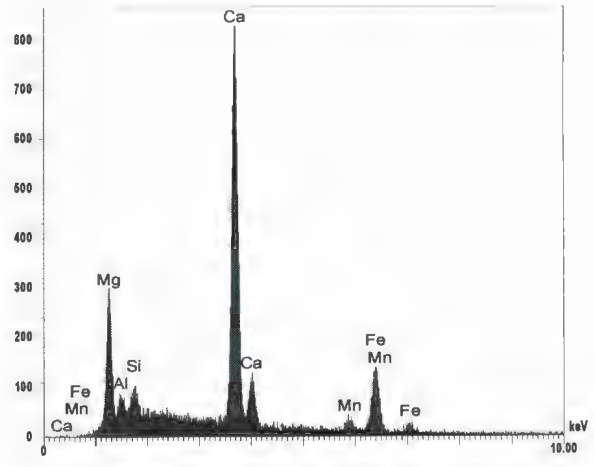
EDS - grain 34: Qtz



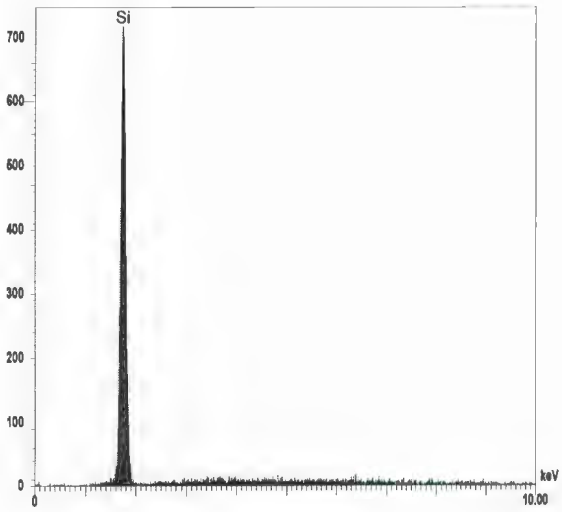
EDS - grain 35: Mg, Ca, Mn, Fe cb



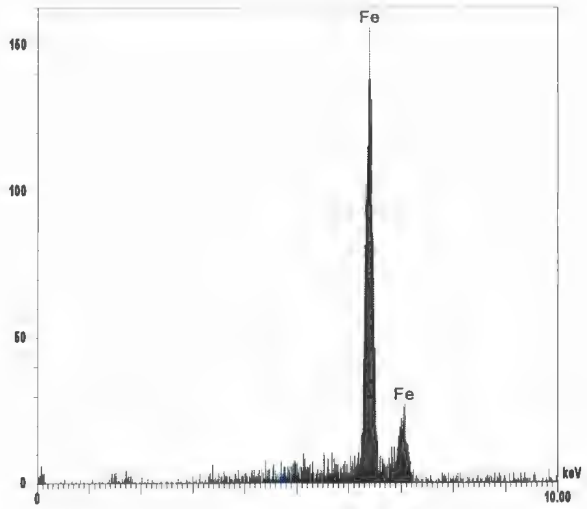
EDS - grain 36: Mg, Ca, Mn, Fe cb



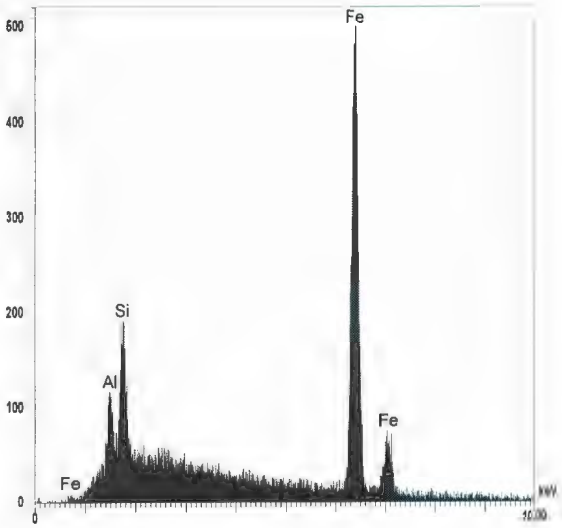
EDS - grain 37: Qtz



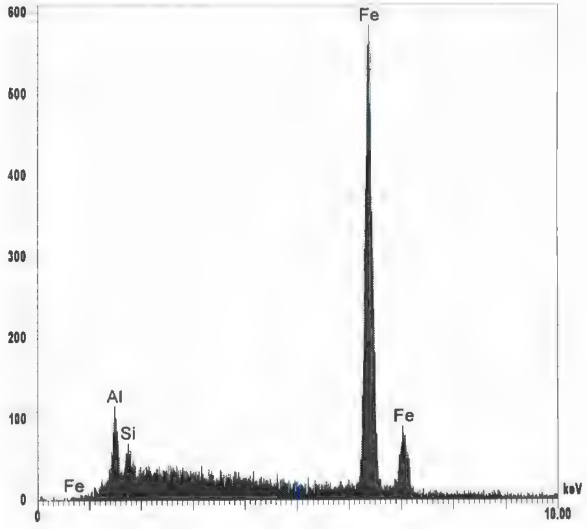
EDS - grain 38: Fe oxide



EDS - grain 39: Am (gru)



EDS - grain 40: Am (gru)



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